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VOL. V.

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OF

APPLIED CHEMISTRY

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ABBREVIATIONS
OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J. .	American Chemical Journal.
Amer. J. Pharm. .	American Journal of Pharmacy.
Amer. J. Physiol. .	American Journal of Physiology.
Amer. J. Sci. . .	American Journal of Science.
Amer. Min. . . .	American Mineralogist.
Anal. Fis. Quim. .	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann. Appl. Biol. .	Annals of Applied Biology.
Ann. Chim. anal. .	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. . . .	Annales de Chimie.
Ann. Falsif. . . .	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Ann. Physik. . .	Annalen der Physik.
Ann. Physique . .	Annales de Physique.
Ann. Report. . .	Annual Reports of the Chemical Society.
Annali Chim. Appl.	Annali di Chimica Applicata.
Apoth. Zeit. . . .	Apotheker-Zeitung.
Arch. exp. Path. Pharm. . . .	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Pharm. . .	Archiv der Pharmazie.
Astrophys. J. . .	Astrophysical Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Bentl. a. Trim. . .	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr. . . .	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J. . .	The Bio-Chemical Journal.
Biochem. Zeitsch. .	Biochemische Zeitschrift.
Brewers J. . . .	Brewer's Journal.
Brit. Assoc. Rep. .	Report of the British Association for the Advancement of Science.
Brit. Med. J. . .	British Medical Journal.
Brit. Pat.	British Patent.
Bull. Acad. roy. Belg.	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Asso. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Imp. Inst. .	Bulletin of the Imperial Institute.
Bull. Soc. chim. .	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. chim. Biol.	Bulletin de la Société de chimie biologique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Chem. and Met. Eng.	Chemical and Metallurgical Engineering.
Chem. Ind. . . .	Chemische Industrie.
Chem. News . . .	Chemical News.
Chem. Soc. Proc. .	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Umschau. .	Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze.
Chem. Weekblad .	Chemisch Weekblad.
Chem. Zeit. . . .	Chemiker Zeitung.
Chem. Zentr. . .	Chemisches Zentralblatt.
Compt. rend. . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J. . .	Dingler's polytechnisches Journal.
D. R. P.	Deutsches Reichs-Patent.
Färber-Zeit. . . .	Färber-Zeitung.
Flück. a. Hanb. .	Flückiger and Hanbury. Pharmacographia.
Frdl.	Friedländer's Fortschritte der Teerfarbenfabrikation.
Gazz. Chim. Ital. .	Gazzetta Chimica Italiana.
Helv. Chim. Acta .	Helvetica Chimica Acta.
J.	Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
Jahrb. Min. . . .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Japan J. Phys. .	Japanese Journal of Physics.

J. Agric. Res. . .	Journal of Agricultural Research.
J. Agric. Sci. . .	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Bact.	Journal of Bacteriology.
J. Bd. Agric. . .	Journal of the Board of Agriculture.
J. Biol. Chem. . .	Journal of Biological Chemistry.
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan.
J. Chim. Phys. . .	Journal de Chimie Physique.
J. Franklin Inst. .	Journal of the Franklin Institute.
J. Gen. Physiol. .	Journal of General Physiology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing .	Journal of the Institute of Brewing.
J. Pharm. Chim. .	Journal de Pharmacie et de Chimie.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan.
J. Phys. Chem. .	Journal of Physical Chemistry.
J. Physiol. . . .	Journal of Physiology.
J. pr. Chem. . .	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers. . .	Journal of the Society of Dyers and Colourists.
J. Tokyo Chem. Soc.	Journal of the Tokyo Chemical Society.
J. Washington Acad. Sei.	Journal of the Washington Academy of Sciences.
Kolloid Zeitsch. .	Kolloid-Zeitschrift.
Mem. Manchester Phil. Soc. . . .	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Met. & Chem. Eng.	Metallurgical and Chemical Engineering.
Min. Mag. . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
P.	Proceedings of the Chemical Society.
Pharm. J. . . .	Pharmaceutical Journal.
Pharm. Zeit. . .	Pharmaceutische Zeitung.
Phil. Mag. . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans. . . .	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Physikal. Z. . . .	Physikalische Zeitschrift.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc. .	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim. . .	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Sci. Proc. R. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitz.	Sitzungsberichte der K. Akademie zu Wien.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Swiss Pat. . . .	Swiss Patent.
T.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
U.S. Pat. . . .	United States Patent.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Z. Elektrochem . .	Zeitschrift für Electrochemie.
Z. ges. Brauw. . .	Zeitschrift für das gesamte Brauwesen.
Z. Kryst.	Zeitschrift für Kristallographie.
Z. Kryst. Min. . .	Zeitschrift für Kristallographie und Mineralogie.
Zeitsch. Nahr. Genussm. . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Physik. . . .	Zeitschrift für Physik.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

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OXYGEN. Sym. O. At.wt. 16.

The first recognition of the *rôle* of oxygen in nature would seem to date from the eighth century. The Chinese philosopher Mao-Khóa then promulgated a theory based on his experiments, that all matter was composed of two fundamental elements, Yang (the strong or primary) and Yin (the weak or secondary). In air both these elements were present combined with elemental fire. The Yang (or more complete air) could be obtained purer by burning in air certain of the metals, sulphur or charcoal, which robbed the air of some of its Yin; whilst Yin, never occurring pure in the air, could be obtained by heating certain minerals (the identity of which is not clear) and especially Hhò-siaō (probably nitre). Mao-Khóa recognised that the Yin of the air was also present in water, though here it was so closely bound to Yang that its separation was difficult. The important part taken by Yin in combustion and respiration was recognised. Leonardo da Vinci was the first European to recognise, towards the end of the fifteenth century, the non-elemental character of the air and to state that only one part of it was concerned in combustion and respiration. Robert Hooke, in Micrographia, published in London in 1665, recognised the same fact, and that the same constituent, or at least a very similar one, was present in nitre. Mayow in 1674 recognised that the *active* constituent of air which supports combustion forms only part of the atmosphere, and that the same substance is present in nitre, and is given off when nitre is heated strongly. Mayow termed this gaseous constituent of air and nitre *spiritus vitalis*, *spiritus nitro-aëreus*, and *pabulum igneo-aëreum*. Borch (1678) carried the work of Mayow further, and Hales (1727) obtained oxygen by heating nitre, and collected the gas over water in nearly theoretical quantity, but failed to recognise its character. Priestley obtained the gas on August 1, 1774, by heating mercuric oxide in a glass vessel by the heat of the sun's rays concentrated on the oxide by means of a burning glass, and gave it the name *dephlogisticated air*. The gas was isolated independently, and almost simultaneously (probably in 1771, though the publication of this result was only made several years later), by the Swedish chemist Scheele, who applied to it the term *empyreal* or *fire-air*. Condorcet soon after suggested the name *vital air*. Lavoisier regarded it as an essential constituent of all acids, and hence gave it its present name *oxygen* (from ὀξύς, acid, and γεννάω, I form). The later discovery that hydrochloric and the other halogen acids contained no oxygen showed that this substance is not necessarily present in acids, but the name has been retained. The discovery of oxygen was the means of leading Lavoisier to the true theory of combustion (*see* Jörgensen, Die Entdeckung des Saurstoffes, Stuttgart, 1909).

Occurrence.—Oxygen is the most abundant and the most widely distributed element in nature. In the free state it occurs, mixed with nitrogen, in the atmosphere, of which it forms about 21 p.c. by volume, and more than 23 p.c. by weight. In the combined state it forms eight-ninths by weight of all the water on the globe, and nearly half of the three chief constituents of the earth's crust, viz. silicious rocks, chalk, and alumina. Most minerals—the chief exceptions being rock salt, fluorspar, blende, galena, and pyrites—contain oxygen in considerable proportions. It is an essential constituent of all animal and vegetable tissues and fluids. It is absorbed in large quantities from the atmosphere by animals and vegetables during respiration, but this abstraction is practically counterbalanced by the oxygen evolved by green foliage under the influence of sunlight.

Preparation.—A. *On the laboratory scale.* Oxygen may be obtained by the action of heat on the oxides of mercury, silver, gold, and platinum; the peroxides of hydrogen, the alkalis, barium, lead, and manganese; the chlorates, bromates, iodates, nitrates, and dichromates of potassium and other bases; it is evolved during some chemical reactions, and during the electrolysis of many substances, notably of water.

Of the modes of preparation most convenient for use in the laboratory, or of interest from historical or theoretical considerations, the following are the principal:—

1. By heating red oxide of mercury it splits up into vapour of mercury (which condenses) and oxygen: $2HgO = 2Hg + O_2$. This reaction

is of interest as being that by which Priestley first obtained oxygen.

2. By heating manganese dioxide to a bright-red heat it gives up one-third of its oxygen: $3MnO_2=Mn_3O_4+O_2$. The oxide is best heated in an iron bottle placed in a furnace, as glass vessels will not stand the high temperature required. 100 parts by weight of the pure peroxide yield 12·3 parts by weight of oxygen.

Manganese dioxide occurs in large quantities in nature as the mineral *pyrolusite*, and thus forms a cheap source for the preparation of quantities of a few hundred cubic feet of oxygen, but the high temperature required makes the process somewhat inconvenient. Pyrolusite usually contains about 70 p.c. of the dioxide, and therefore gives a lower yield of oxygen than that indicated by the equation.

3. Potassium chlorate is a very convenient and economical source for small quantities of oxygen for lecture and laboratory purposes. When gradually heated in a hard glass retort or flask, this salt melts at about 360°–370°, and at about 370°–380° evolution of oxygen commences. After some time the fused mass thickens from the formation of the perchlorate, which, at a still higher temperature, is also decomposed. Ultimately, therefore, potassium chloride alone remains in the generating flask, the whole of the oxygen having been given off according to the equation: $2KClO_3=2KCl+3O_2$. 100 parts by weight of chlorate yield 39·16 parts by weight of oxygen, or 1 oz. of chlorate gives 1·8 gallons of the gas. The oxygen obtained is very pure.

The temperature required in this decomposition is too high for convenient use, as the glass vessels employed in the preparation of the gas often soften under the great heat, and yield to the pressure of the contained gas. When metallic vessels are used the heating must be very carefully watched, since the decomposition being exothermic (*i.e.* heat being evolved during the reaction), when once decomposition has set in, the evolution of gas is liable to become very violent. If the potassium chlorate be mixed with about one-eighth its weight of some non-fusible oxide, such as oxide of copper, oxide of iron, or manganese dioxide, the evolution of oxygen takes place at about 240°, or considerably below that at which the salt fuses, and is much more regular. The addition of a little spongy platinum answers the same purpose.

The gas prepared in this way almost invariably contains traces of chlorine, which are removed, when necessary, by passing the gas through a solution of caustic soda.

Commercial manganese dioxide (pyrolusite) is sometimes adulterated with coal-dust. If such dioxide is heated with potassium chlorate the coal-dust burns—often with explosive violence—at the expense of the oxygen of the chlorate, and this has been the cause of fatal accidents. It is, therefore, advisable to test the dioxide before use by heating a small quantity in a test tube with some chlorate.

The action of these oxides in facilitating the decomposition of the potassiun chlorate is probably due to the transient formation of higher oxides of extreme instability. The oxides which show this action most markedly are those which form unstable higher oxides. The action of spongy platinum is less clear, but is probably connected with the tendency of that substance to condense oxygen on its surface.

4. By heating a concentrated solution of bleaching powder (or any hypochlorite) to which a small quantity of oxide of cobalt has been added, it is resolved into calcium chloride and oxygen: $2CaOCl_2+4CoO=2CaCl_2+2Co_2O_3$ and $2Co_2O_3=4CoO+O_2$. The decomposition is shown in two stages to exhibit the action of the oxide of cobalt. It is not necessary to use preformed oxide of cobalt, as any salt of cobalt will answer the same purpose. The oxides of copper and nickel are similar in their action. Instead of a solution a thick paste of bleaching-powder and water may be used if a small quantity of paraffin oil is added. The oil, floating on the surface of the pasty liquid, prevents the frothing which would otherwise take place. The best temperature for the evolution of gas is about 70°–80°, at which a steady stream may be obtained. For a study of the conditions determining the velocity of evolution of oxygen from bleaching powder, *see* Bell, Zeitsch. anorg. Chem. 1913, 82, 145.

Another modification of this method is to pass a stream of chlorine into boiling milk of lime to which a small quantity of a salt of copper, cobalt, or nickel has been added. Oxygen gas is given off according to the equation $2Cl_2+2Ca(OH)_2=2CaCl_2+2H_2O+O_2$.

5. From various peroxides—

(*a*) When an intimate mixture of 3 mols. barium peroxide (2 parts by weight) and 1 mol. potassium dichromate (1 part by weight) is treated with dilute sulphuric acid, oxygen is abundantly evolved at ordinary temperatures (Robbins, Pharm. J. [ii.] 5, 436).

(*b*) If 500 c.c. of commercial hydrogen peroxide (10 p.c. solution) are introduced into a suitable generating flask, and a solution of 25 grms. of potassium permanganate in 500 c.c. of water, mixed with 25 c.c. concentrated sulphuric acid, is allowed to flow gradually into the mixture from a dropping funnel, oxygen will be rapidly evolved without the application of heat, the amount of oxygen obtained from these quantities being about 10 litres.

(*c*) Baumann recommends (Zeitsch. anorg. Chem. 1890, 79) charging a Kipp apparatus with pieces of pyrolusite of 2–4 mm. diameter and using as the activating liquid commercial hydrogen peroxide to which, while well cooled, 150 c.c. of strong sulphuric acid has been added per litre. The evolution of the oxygen is steady and continuous. Neumann recommends the use of cubes made from 2 parts barium peroxide, 1 part pyrolusite, and 1 part gypsum with hydrochloric acid of sp.gr. 1·12 as activating liquid, but the oxygen evolved by this method contains traces of chlorine.

(*d*) If water is dropped on to broken pieces of fused potassium, sodium or potassium-sodium peroxide, a steady stream of oxygen is evolved. Walter recommends fusing 100 grms. sodium peroxide, 100 grms. potassium nitrate, and 25 grms. magnesia; hydrochloric acid is then dropped on to the cold broken-up mass.

(*e*) If a mixture of equal parts of sodium peroxide and a salt containing water of crystallisation, such as sodium sulphate, is gently heated, oxygen is evolved in a steady stream.

6. On passing a mixture of steam and

chlorine through a red-hot porcelain tube, filled with fragments of porcelain to increase the heating surface, the chlorine combines with the hydrogen of the water and oxygen is liberated: $2H_2O+2Cl_2=4HCl+O_2$.

7. By the electrolysis of a solution of sodium hydroxide or of water slightly acidulated with sulphuric acid, the water is resolved into hydrogen and oxygen, the latter appearing at the positive pole: $2H_2O=2H_2+O_2$. This forms a convenient method of obtaining small quantities of pure oxygen, such as are required in gas analysis.

8. Oxygen may be prepared from such highly oxidised compounds as peroxides of lead and manganese, potassium dichromate and permanganate, &c., by the action of sulphuric acid. These are, however, seldom used as sources of gaseous oxygen, but are very useful as oxidising agents. Thus hydrochloric acid, when treated with sulphuric acid and potassium permanganate, is oxidised to hypochlorous acid, and alcohol treated with sulphuric acid and manganese dioxide yields aldehyde and water. The following equations represent the changes which take place when manganese dioxide and potassium dichromate are respectively treated with sulphuric acid:

$$2H_2SO_4+2MnO_2=2MnSO_4+2H_2O+O_2$$

and $$8H_2SO_4+2K_2Cr_2O_7=2K_2SO_4+2Cr_2(SO_4)_3+8H_2O+3O_2$$

The change is rendered visible in the latter case by the formation of a deep-green salt of chromium, the solution being previously of a red colour.

9. When fresh leaves, such as mint or parsley, are exposed to the influence of sunlight in an inverted cylinder filled with water saturated with carbon dioxide and standing in a basin of the same liquid, oxygen appears after a time in minute bubbles on the leaves, and collects in the upper part of the jar. This method of liberating oxygen is of interest as being that which occurs in nature, by means of which the loss of atmospheric oxygen continually taking place from combustion and respiration is replaced.

B. *On the industrial scale.* 1. The first method proposed for obtaining oxygen on the large scale was the ignition of nitre, and this method, in various modifications, has formed the basis of several patents. The first oxygen patent occurring in the records of our Patent Office, is No. 12536, S. White, 1849. But the oxygen so obtained was contaminated with oxides of nitrogen, and this method has not proved advantageous. It deserves mention, however, as being the means by which Priestley first obtained impure oxygen in 1771. He then believed the gas to be 'fixed air' (carbon dioxide), and only recognised his mistake 3 years afterwards, when he obtained oxygen from mercuric oxide.

2. By heating manganese dioxide. This was formerly one of the cheapest methods of preparing oxygen on the commercial scale.

3. By heating a mixture of potassium chlorate and about one-eighth of its weight of manganese dioxide. Though more costly than the last-named, this method is more easily carried out, and was, until within the last 30 years, almost exclusively employed in the preparation of the considerable quantities of oxygen used for lime-light purposes.

4. By the decomposition of sulphuric acid by heat: $2H_2SO_4=2SO_2+2H_2O+O_2$. The sulphuric acid is allowed to drop on red-hot surfaces, and is thus decomposed. If the oxygen alone is wanted, the emergent gaseous mixture is passed over media suitable for the absorption of the water and sulphur dioxide. As a method for the preparation of oxygen only this process has not found much favour, but it has been used in the preparation of sulphur trioxide, where, the water being removed by a desiccating agent, a mixture of sulphur dioxide and oxygen in the desired proportions is at once obtained. It is the process suggested by Squire in his patent for the manufacture of sulphur trioxide (Eng. Pat. 3278, 1875).

5. By the dialysis of air. Many attempts have been made to utilise the laws of diffusion of gases through porous septa, discovered by Graham, or the property of caoutchouc when in thin layers to allow oxygen to pass through it more readily than nitrogen. Several patents have been taken out for processes of this kind, but with no practical success, and the phenomena do not seem likely to lend themselves to the production of oxygen on the large scale.

6. Better success has attended the endeavour to make use of the greater solubility of oxygen than of nitrogen in water or other solvents. Mallet, who took out a patent for this process (Eng. Pat. 2137, 1869), compressed the air over water. The coefficient of solubility of oxygen in water is about twice that of nitrogen. The oxygen was, therefore, dissolved in greater proportion than the nitrogen, and when the excess of pressure was removed and the dissolved gases extracted by the aid of a vacuum pump, the amount of oxygen in the gaseous mixture was greater than in air. This mixture was then repeatedly subjected to the same treatment, when, after about eight absorptions, nearly pure oxygen was obtained. The following table, given by Mallet (Dingl. poly. J. 199, 112), shows the composition of the gaseous mixture at each successive stage of the operation:—

Atmospheric air	Composition after successive absorptions							
	1	2	3	4	5	6	7	8
N=79	66·7	52·5	37·5	25·0	15·0	9·0	5·0	2·7
O=21	33·3	47·5	62·5	75·0	85·0	91·0	95·0	97·3

This process was used by Phillips in 1871–72 to obtain oxygen for his experimental lighting of part of Cologne by special oxygen-fed oil lamps, but beyond this does not appear to have been practically applied.

7. By the alternate oxidation and de-oxidation of cuprous chloride. Cuprous chloride, if exposed to air, and especially to moist air, is oxidised to cupric oxychloride, and this, when heated to dull redness, gives off oxygen, and is reconverted into cuprous chloride.

$$(a)\ 2Cu_2Cl_2+O_2=2Cu_2OCl_2$$
$$(b)\ 2Cu_2OCl_2=2Cu_2Cl_2+O_2$$

Mallet obtained patents (Eng. Pats. 2934, 1865, and 3171, 1866) for the practical utilisation of this method as a continuous process for

obtaining oxygen from the air, but it has not been found economically available on the large scale.

8. By the alternate formation and decomposition of alkaline manganates. When an oxide of manganese is mixed in suitable proportions with a caustic alkali (potash or soda), and is subjected to the action of air at a moderately high temperature, an alkaline manganate is formed. If this manganate is then heated to a bright-red heat, and a current of steam passed over it, it is resolved into its original constituents with evolution of oxygen (C. M. Tessié du Motay and C. R. Marechal, Eng. Pat. 85, 1866).

$$2MnO_2+4NaOH+O_2(air)=2Na_2MnO_4+2H_2O$$
$$2Na_2MnO_4+2H_2O=Mn_2O_3+4NaOH+3O$$
$$Mn_2O_3+4NaOH+3O(air)=2Na_2MnO_4+2H_2O$$

The mixture was introduced into horizontal retorts, which were heated to a dull red heat while a current of air was passed through. After oxidation was complete the supply of air was cut off, the retorts were heated to a bright red heat and a current of steam admitted, when oxygen was evolved. The retorts were then allowed to cool again to a dull red, the passage of air again commenced, and so on. The mixture was said to undergo no deterioration, and a continuous and very economical method of obtaining oxygen seemed attained. Works were erected, and the process carried out on the large scale at Paris, Lille, Brussels, Vienna, and New York, and large quantities of oxygen were made. A large part of Paris was laid with a double system of piping with the intention of lighting that city with the oxy-hydrogen light, and the New York Company carried out by the same light the lighting of the works during the building of the Brooklyn bridge. But it was found in practice that the mixture did deteriorate, the yield of oxygen rapidly diminishing, and finally almost ceasing. This was probably due to the difficulty of maintaining the intimate mixture of the easily fusible, hygroscopic and very soluble soda with the manganic oxide, the former settling to the bottom through the combined effect of the heat and steam used.

Bowman (Eng. Pat. 7851, 1890) claimed to have overcome this difficulty by making the alkaline manganate in a granular form and dusting over the granules, whilst still in a plastic condition, with oxide of copper. Parkinson (Eng. Pat. 14925, 1891) claimed improved modes of preparation of the material together with the use of a vacuum in place of steam to cause the evolution of the oxygen. The manganate material, in upright iron retorts, was heated to about 1200°, and air pumped in under pressure to effect oxidation; the pumps were then automatically reversed and the oxygen drawn off under greatly reduced pressure. Fanta's claim (Eng. Pat. 3034, 1891) mainly consisted in increased stability of the material by the use of excess of caustic soda, and Webb's resembled Bowman's, except that the pieces of manganate material were dusted over with manganese peroxide instead of with oxide of copper. In Chapman's process (Eng. Pat. 11504, 1892) 'oxide of manganese (or the like) in a powdered form is kept suspended in fused soda (or the like) so that the charge is practically in the condition of a liquid,' and the alternate supplies of air and steam were driven into the liquid at the bottom, thereby keeping the oxide in a state of suspension. But though these modifications have been tried on the practical scale, none of them proved commercially successful.

9. Kassner (Eng. Pat. 11899, 1889) found that when an intimate mixture of lead oxide and chalk is heated to 600° in contact with the air, a calcium plumbate Ca_2PbO_4 is formed. If this plumbate is then introduced into a solution of potassium or sodium carbonate it is decomposed, an insoluble precipitate of calcium carbonate and lead peroxide is formed, and caustic potash or soda remains in solution. This is removed by decantation, and the precipitate washed. The precipitate, in which the lead peroxide is, of course, the active part, may then either be used directly as an oxidant, or it may be introduced into a decomposing vessel, dried with superheated steam, and heated to about 500°, when oxygen is evolved, the mixture of lead oxide and calcium carbonate left being then ready for regeneration. The decomposition of the plumbate may also be effected by suspending it in water and treating with carbonic acid. The following equations indicate the reactions taking place:

$$2CaCO_3+PbO+O(air)=Ca_2PbO_4+2CO_2$$
$$Ca_2PbO_4+2Na_2CO_3+2H_2O=4NaOH+2CaCO_3+PbO_2$$
$$2CaCO_3+PbO_2=2CaCO_3+PbO+O$$

The complexity of the process and the large amount of labour entailed by it, offer little chance of its being practically applicable, except possibly in chemical works, where it may be used in conjunction with the manufacture of caustic alkali, and even here its economy is very doubtful.

The decomposition of the plumbate into lime and lead peroxide may also be effected *in situ* by means of a current of moist furnace gases at 80°–100°, and the oxygen then liberated by raising the temperature. The great changes of temperature, however, thus involved, render the method impracticable, and in addition the sulphur impurities in the furnace gases rapidly deteriorate the mixture.

Salamon (Eng. Pat. 6553, 1890) proposed to decompose the calcium plumbate without removing it from the producer in which it is formed by allowing the temperature to fall 'to a certain point,' and then introducing a current of pure carbon dioxide. The following reaction then occurs:

$$Ca_2PbO_4+2CO_2=2CaCO_3+PbO+O$$

This necessitates the use of at least four times the volume of carbon dioxide as of oxygen obtained, a condition which at once puts the process out of the question as a technical and economical one. It has been suggested that the quantity of pure carbon dioxide required may be largely reduced by carrying out the earlier part of the reaction by means of the carbon dioxide in furnace gases, and using it pure only at the last. But the drawbacks so introduced neutralise any advantage.

10. By the alternate formation and decomposition of barium peroxide. In 1851 Boussingault found that when barium oxide (baryta) is heated to a dull red heat in a current of air it is converted into barium peroxide, and that at

a higher temperature this peroxide is again resolved into barium oxide and oxygen. But his attempts to utilise this reaction as a practical and economical source of oxygen failed owing to the fact that after a few oxidations and deoxidations the baryta lost its power of re-absorbing oxygen. Many other attempts were made to overcome this difficulty, but for long without success. In 1879, however, the MM. Brin frères were more successful, and took out a patent for the process (Eng. Pat. 1416 of 1880). Further improvements were made under the auspices of the company formed to develop and work the patents, and the process was made practical and economical, and was worked on a large scale at various places.

The permanence of the baryta is mainly dependent on its physical condition, the use of reduced pressure during deoxidation, and consequent avoidance of excessively high temperatures, and the careful purification of the air used. It was found possible to dispense with change of temperature in the reaction, change of pressure being alone trusted to for determining the respective phases of oxidation and deoxidation. Neither the oxidation nor the deoxidation is as complete as when two temperatures are used, and the yield per operation is much less. But the duration of the operation was reduced from about 4 hours to 8–15 mins., and the total daily yield therefore largely increased. At the same time the operation was much simplified, the wear and tear of furnace, retorts, &c., greatly reduced, and the fuel required lessened. Labour was also economised, the multiplied reversals of cocks, &c., necessitated by the single-temperature method of working being effected automatically by reversing gear designed by K. S. Murray. The labour required was therefore little more than that needed for stoking the furnace, and oiling and supervising the pumps, &c. The oxygen obtained had a purity of about 93–96 p.c.

For a producer capable of delivering 10,000 cubic feet of oxygen per 24 hours the consumption of coke in the furnaee was about 12–15 cwt. per day, and for plant of that or smaller size the pump power required was about 1 I.H.P. per 1000 feet of oxygen produced per day, the ratio decreasing for larger plants.

It is necessary that the barium oxide should be as hard and as porous as possible, and this is best obtained by igniting the nitrate. The nitrate fuses and decomposition soon commences with evolution of a mixture of oxygen and oxides of nitrogen. This action continues for about 2–3 hours, during which time the contents of the crucible remain in ebullition. A porous mass is then left, which is heated for another hour to complete, as far as possible, the decomposition. In this way a very hard but also very porous baryta is obtained.

This process was thoroughly practical and economical, and large numbers of plants were erected all over the world and worked successfully for many years. It was described in detail with illustrations of plant in the first edition of this dictionary (*see* also K. S. Murray, Proc. I. Mech. E. 1890, 131; Thorne, J. Soc. Chem. Ind. 1890, 246). In the last few years the process has been largely superseded by the still cheaper liquid air process, which also produces oxygen of greater purity (v. *infra*).

Cost of production.—It is very difficult to obtain data of the cost of production of oxygen under the earlier methods described, but the following figures probably approximate to the cost per 1000 cubic feet:—from chlorate 8*l.*–10*l.*; from pyrolusite 4*l.*–6*l.*; from sulphuric acid 2*l.* 10*s.*–3*l.* (probably higher when only the oxygen and not the sulphur dioxide is utilised); by the Tessié du Motay process 3*l.*–4*l.*; by the Brin process 7*s.*–12*s.* No authentic data of the cost of producing oxygen by dialysis or by solution in water are obtainable, but it would probably be *at least* as high as that by the Tessié du Motay process. In the Kassner process the cost depends largely on the amount realised by the sale of the caustic alkali, but would certainly be prohibitive for technical purposes. For cost by the liquid air and electrolysis processes, v. *infra*.

Properties.—The International Committee on Atomic Weights has adopted O=16 as the standard of comparison for all atomic weights, and under this scale H=1·008 (1·0076 Morley). Oxygen is a colourless, tasteless, and inodorous gas, of sp.gr. 1·1056 (air=1): at 0° and 760 mm. pressure a normal litre of gas weighs 1·42905 grms. (1·42893 at 0° and 760 mm., and 0·29071 grm. at 1067·4° and 760 mm., Jacquerod and Perrot, Compt. rend. 1905, 140, 1542; 1·42889 at 0°, 760 mm., sea-level and latitude 45°, Moles and Gonzalez, *ibid.* 1921, 173, 355), and at 30 ins. pressure and 15·5° 100 cubic ins. weigh 34·206 grs. 1 grm. of oxygen measures 0·6997 litre and 1 lb. 11·84 ft. Its absolute viscosity at 23° and 760 mm. pressure is $n+10^7=2042{\cdot}35$ (Kia-Lok Yen, Phil. Mag. 1919, [vi.] 38, 582). Oxygen also occurs in an active allotropic form called *ozone*, which is treated of in a separate article (*v.* OZONE).

Oxygen normally acts as a divalent element, but in many compounds, especially in certain organic compounds having somewhat basic characteristics, acts as a tetrad. When examined through very thick and highly compressed layers, gaseous oxygen has a slight blue tinge of colour. It is sparingly soluble in water. As with all gases, the quantity of oxygen dissolved by water depends on the tension of the oxygen in the atmosphere in contact with the water. Thus pure water shaken up in contact with pure oxygen will absorb nearly five times as much oxygen as it would when shaken up, at the same temperature and under the same pressure, with air—which only contains 20·9 p.c. by volume of oxygen. The following table gives the coefficients of solubility (*i.e.* the volume of oxygen absorbed by one volume of water when shaken up with pure oxygen under 760 mm. pressure) at different temperatures as determined by different observers:

Temperature	Coefficient of solubility					
	Bunsen (1855)	Dittmar	Roscoe and Lunt	Winkler (1861)	Bohr & Bock (1891)	Fox (1905)
0°C.	0·0411	—	—	0·0489	0·0496	0·0492
10°	0·0325	0·0383	0·0377	0·0380	0·0390	0·0384
20°	0·0284	0·0312	0·0308	0·0310	0·0317	0·0314
30°	—	—	—	0·0262	0·0268	0·0267
40°	—	—	—	—	0·0233	0·0233
50°	—	—	—	—	0·0207	0·0209

These numbers multiplied by 1000 give the number of c.c. oxygen absorbed by a litre of water from pure oxygen.

Winkler gives the following formula for calculating the coefficient of solubility (β) of oxygen in water at any temperature (t):

$$\beta = 0{\cdot}04890 - 0{\cdot}0013413t + 0{\cdot}0000283t^2 - 0{\cdot}00000029534t^3$$

Fox (Trans. Far. Soc. 1909, [v.] 68-81) gives the formula:

$$\beta = 0{\cdot}04924 - 0{\cdot}0013440t + 0{\cdot}000028752t^2 - 0{\cdot}0000003024t^3$$

Rain-water is very nearly saturated with oxygen when its temperature, as collected, is below 15°. During the summer months the dissolved oxygen is always less than the saturation quantity, sometimes by as much as 25 p.c.

The coefficient of solubility of oxygen in alcohol at 0° is 0·2337; at 20° it is 0·2201 (Timofejeff), so that oxygen is much more soluble in alcohol than in water.

Nearly all natural waters contain oxygen in solution and can only be freed therefrom by prolonged boiling *in vacuo*. This dissolved oxygen, though small in amount, is the source from which fish obtain the oxygen necessary to sustain life.

The solubility of oxygen in sea water at 16° is about 78 p.c. of its solubility in pure water (Clowes and Biggs). All saline solutions dissolve less oxygen than pure water. The gas is very sparingly soluble in a strong solution of ammonium chloride.

For the solubility of oxygen in various organic solvents see Fischer and Pfleiderer, Z. anorg. Chem. 1922, 124, 61.

Oxygen, though long regarded as a permanent gas, was liquefied in 1877 by Pictet at a pressure of 320 atmospheres, and a temperature of −140°. Cailletet had previously observed the formation of a mist due to liquefaction when oxygen at −29° under a pressure of 300 atmospheres was allowed to expand suddenly. Olszewski in 1883 showed that the *critical temperature* of oxygen (*i.e.* the temperature above which no amount of pressure will liquefy it) is −113°, the pressure needed to liquefy it at that temperature being 50 atmospheres, and this was confirmed by Wroblewski and by Dewar in 1885. According to Cardoso (Arch. Sci. phys. nat. 1915, [iv.] 39, 400) the critical pressure is 49·30 atmos. and the critical temperature −118°. According to Kamerlingh Onnes the critical data are −118·84 and 49·713 atmospheres.

Liquid oxygen is a pale steel-blue transparent and very mobile liquid showing a clear meniscus (Dewar; Olszewski) boiling at −182·5° at 760 mm. pressure. When the pressure is reduced or removed, evaporation takes place so rapidly that a part of the oxygen is often frozen. Solidification takes place under 9 mm. pressure at −211·5° (W.), under 172 mm. at −219° (Dewar, Roy. Soc. Proc. 1911, 85, 589). This latter temperature is therefore the lowest obtainable by the evaporation of liquid oxygen. Travers, Sinter and Jacquerod (Proc. Roy. Soc. 1902, 70, 484) found the b.p. of oxygen to be −182·8° at 760 mm., −185° at 600 mm., −188·5° at 400, and −193·8° at 200 mm. The vapour pressure of oxygen at temperatures in the neighbourhood of 57°–90° (abs.) may be expressed by the equation $\log p = A/T + B + CI$ (p in atm.) with A = −419·31, B = 5·2365, C = 0·0648 (Cath.). Dewar obtained solid oxygen as a hard, doubly refracting pale blue crystalline mass by cooling liquid oxygen in a spray of liquid hydrogen. Its m.p. is −219° under a pressure of 1·12 mm. The density of liquid oxygen is 1·1181 at −182·5°, 1·1700 at −195·5°, 1·2386 at −210·5°, and that of solid oxygen 1·4256 at −252·5° (Dewar) corresponding to the general formula (for liquid and solid) $d = 1{\cdot}5154 - 0{\cdot}00442T°$ (where T° = absolute temperature). 781·8 volumes of oxygen at 0° and 760 mm. are contained in 1 volume of liquid oxygen at −182·5°. The latent heat of vaporisation of liquid oxygen varies with the temperature (Alt), at 760 mm. pressure (*i.e.* −182·5°) it is 50·97 cals., at −205° it is 55·5 cals. The specific heat between −200° and −183° is 0·347±0·014. The vapour density at −182° is normal. The refractive index of liquid oxygen is 1·2236. Liquid oxygen absorbs nitrogen readily, dissolving at −190·5° 380 times its volume, or 42 p.c. of its weight of gaseous nitrogen, the b.p. being thereby reduced to −188·8°. This was probably the cause of the discrepancies in the boiling-points given by the earlier observers. Liquid oxygen is a very perfect insulator, and is also comparatively inert in its chemical properties. Phosphorus, potassium, sodium, &c., may be immersed in it without any action taking place (Dewar).

When liquid oxygen is subjected to the action of strong light, and particularly of the ultra-violet rays, some of it is converted into ozone (Dewar) (*cf.* Weigert, Ber. 1913, 46, 815). It is also ozonised by α-rays. It is diathermanous, a non-conductor of electricity, but is strongly magnetic, its magnetic moment being 1 when iron is taken at 1000. The magnetic susceptibility of liquid oxygen at the freezing-point is 1·3 times as great as that of the solid. Its susceptibility is diminished or temporarily suspended by elevation of temperature. Oxygen is the least refractive of all gases; it gives a characteristic though not very strong absorption spectrum, but to obtain this it is necessary to view the source of light through great thicknesses of liquid or through the highly compressed gas. The spectrum first appears in the form of a number of fine lines, but as the pressure is increased or a layer of liquid oxygen is employed, it shows a number of broader and shaded dark bands, with almost complete absorption in the violet and ultra-violet. Six absorption bands have been observed, two in the red corresponding to the A and B Fraunhofer lines. The absorption spectrum of liquid oxygen is practically identical with that of gaseous oxygen. Oxygen shows a luminous spectrum in a Geissler tube containing a bright band in the red, two in the green, and one in the blue, but the spectrum varies under varying conditions.

The chemical activity of air depends upon the oxygen it contains, air being simply, in its chemical relations, oxygen diluted with nitrogen. Free oxygen, whether diluted with nitrogen or not, manifests considerable chemical activity, even at ordinary temperatures, this activity increasing with rise of temperature. There

are only few elements—viz. fluorine, chlorine, bromine, iodine, silver, gold, platinum, neon, argon, and helium—which do not unite *directly* with oxygen. Most of the non-metallic elements unite with oxygen to form anhydrous acids. Of the exceptions, hydrogen forms a neutral oxide (water), whilst no oxides of fluorine, argon, neon, or helium have yet been obtained.

Phosphorus combines with oxygen at ordinary temperatures, as do also moist iron, moist lead, moist saw-dust, and many metallic compounds such as cuprous chloride, manganous hydroxide, ferrous hydroxide, &c. This oxidation at ordinary temperatures is called *autoxidation*, and substances undergoing autoxidation often induce the oxidation of other substances present which otherwise would not oxidise spontaneously. The alkali metals, especially rubidium, are especially active in this way. In many cases ozone is simultaneously produced. Light, and particularly sunlight, greatly assists oxidation by gaseous oxygen. Potassium and sodium are at once attacked by dry oxygen at ordinary temperatures, becoming coated with their respective oxides. The majority of metals remain bright under similar conditions, but many become oxidised when moisture is present. In some of the metals oxidised by exposure to air the first coating of oxide formed acts as a protective covering and prevents further oxidation, as is the case with lead. In others, however, the oxide first formed gradually becomes converted into a higher oxide and may then give up part of its oxygen to the metal in contact with it, and the oxidation is thus propagated through the mass of the metal. The rusting of iron is not a simple case of oxidation. Some metals which in their ordinary condition are comparatively inert towards oxygen combine with it readily at ordinary temperatures when they are in a finely divided state, offering a very large surface for chemical action. Thus lead or antimony when obtained by the ignition of their tartrates, and iron, nickel, cobalt, and copper, when reduced from their precipitated oxides in a current of hydrogen at a low temperature, all ignite spontaneously in contact with air or oxygen, and when in this finely divided state are therefore often termed *pyrophori*. Silver, gold, and platinum are not acted on directly by oxygen at any temperature. Some metals in a molten state absorb considerable quantities of oxygen which is given out again wholly or in part when the metal solidifies. 10 grms. of molten silver at 1020° absorb about 20 c.c. oxygen (*v.* Donnan and Shaw, J. Soc. Chem. Ind. 1910, 987).

Molten platinum and palladium also absorb oxygen. Heated at 450° silver gradually absorbs (*occludes*) about 5 times its volume of oxygen, gold 35–45, platinum 65–75, and palladium about 500 (7 p.c. by weight). Platinum black absorbs about 100 times its volume of oxygen and palladium sponge 1000, of which the whole is not given up again below a red heat. Wood charcoal absorbs oxygen at ordinary temperatures—about 18 times its volume (Goldstein)—but this absorptive power increases enormously at very low temperatures. At −185° 1 c.c. absorbs 230 c.c. of oxygen with the evolution of 34 cals., and this action may be employed to produce an oxygen vacuum, the pressure being reduced to that of a Geissler tube (Dewar).

The activity of oxygen is increased greatly by increase of temperature, and with most substances (except under the conditions already mentioned) an initial heating is necessary to start free oxidation, the heat evolved during oxidation being then sufficient to maintain it. Thus iron heated to bright redness in an atmosphere or stream of oxygen takes fire and burns brightly. A mixture of oxygen and hydrogen may be kept at ordinary temperatures for any length of time without change, but if the temperature of any part of the mixture be raised to bright redness—either by the electric spark, by the presentation of a flame or by other means—ignition at once takes place with explosive force throughout the whole mass. Under certain circumstances, however, this combination may be effected at ordinary temperatures. Thus, if a piece of clean platinum foil be hung in the mixture, combination takes place gradually at ordinary temperatures. This appears to be due to the power possessed by palladium, platinum, and some other substances of condensing gases and especially hydrogen on their surfaces, the activity of the gases so condensed being thereby greatly increased. If platinum or palladium black or sponge is used instead of foil, the action is so much increased that the heat evolved in the combination soon raises the temperature of the metal to the ignition-point of the gaseous mixture, and ordinary combustion ensues. This effect has been taken advantage of in the *Döbereiner* lamp (named after the investigator who first noticed this property of platinum) wherein a piece of spongy platinum is suspended over a jet connected with an automatic hydrogen-generating vessel. When the tap is turned on, the jet of hydrogen becoming mixed with air and at the same time impinging on the spongy platinum, oxidation takes place rapidly, the platinum soon becomes red hot and ignites the jet of hydrogen. Similar effects are produced with oxygen (or air) and gaseous hydrocarbons.

Various substances which expose large surfaces to air (or oxygen) become gradually heated through slow oxidation or combustion, and, if the heat cannot get away, ignition eventually occurs. Thus oily or greasy woollen and cotton rags and refuse are capable of absorbing oxygen fairly rapidly, and if present in any quantity the heat produced may accumulate and cause spontaneous combustion, and this action is a not infrequent cause of fires in factories. A similar generation of heat and eventual 'spontaneous combustion' often arises from the storing of moist hay in hayricks, and from the storage of damp coal in ships or heaps. The allegation that the ignition of coal is due to the oxidation of pyrites has been disproved by the work of Richters and Lewes, who have shown that the heat is generated by the absorption of oxygen and its action on the bituminous constituents of the coal.

Dixon, Baker, Traube, and others have shown that even at high temperatures the presence of a trace of moisture is necessary for free oxidation (combustion), and that in *absolutely* dry oxygen, sulphur and phosphorus can be distilled, and carbon made red-hot without

combustion taking place. A jet of burning dry carbon monoxide is even extinguished when introduced into pure and absolutely dry oxygen. The presence of the minutest trace of moisture is, however, sufficient to restore to oxygen its activity.

In ordinarily dry oxygen all substances which burn in air burn with much greater brilliancy, and many substances which do not burn in air burn vividly in oxygen. Thus iron, zinc, &c., if the ignition is started by a portion being raised to a white heat in an atmosphere of oxygen, continue to burn with great brilliancy and with the production of much heat. The actual amount of heat given out during the complete oxidation of any substance is the same whether the combustion is slow or rapid, and is carried on in air or in oxygen. But it is quite different in regard to the temperature developed, this depending on the concentration of the heat, and so being higher the more rapid the combustion and the less extraneous matter is present to absorb the heat. Thus, when phosphorus is burned in oxygen, the temperature produced is very high, and the combustion takes place with dazzling brilliancy. The temperature of a hydrogen or a coal-gas flame burning in oxygen is very much higher than that of a similar flame burning in air. The temperature of a flame of hydrogen burning in oxygen is 2800°; of carbon monoxide 2600°; and of acetylene 3000°. These facts have been utilised in the construction of the oxy-hydrogen and oxy-acetylene blowpipes for obtaining very high temperatures (v. *infra*). If coal-gas is substituted for the hydrogen, a very hot flame is still obtained, but the temperature is not as great as when hydrogen is employed. 16 grms. of oxygen combining with hydrogen to form water evolve 68,400 cals.

Oxygen is the only gas capable of supporting respiration, and forms the life-maintaining constituent of air. In the pure state it may be inhaled for a time with impunity, and acts as a mild tonic or exhilarant. But its long-continued respiration is harmful, feverishness and weakness being produced; and it becomes poisonous if breathed under pressure. Dr. Richardson kept a rabbit in an atmosphere of pure oxygen at a temperature of 23·9° for 3 weeks. It ate voraciously all the time, but became so emaciated from inability to assimilate new material fast enough to supply waste that it was found necessary to discontinue the experiment. At 7·2° the rabbit became speedily narcotised, and would have died had it not been removed. Richardson found that cold-blooded animals were very little affected by being introduced into an atmosphere of oxygen, whilst most warm-blooded animals (dogs, cats, guinea-pigs, &c., but not the rabbit) speedily showed strong febrile symptoms (Asclepiad 1887–89). Some observers had noticed very decided narcotic effects produced on animals under these conditions, but Richardson ascertained that this is due to the oxygen becoming vitiated by repeated inhalations. He found that when the same oxygen was used over and over again, although purified from carbonic acid, &c., by passage over caustic potash, sulphuric acid, &c., the animals became speedily narcotised, but that when a continuous stream of fresh oxygen was employed this was not the case. This 'devitalising' of the oxygen appears to be due to traces in the exhaled gases of some compound which is not removed by the ordinary methods of purification. The electric discharge very quickly re-vitalised the vitiated oxygen. Flesh was found to decompose more readily in devitalised than in pure oxygen. At low temperatures, and at very high ones, however, oxygen is decidedly narcotic in its effect.

But although in health the continued inhalation of nearly pure oxygen is detrimental, its use where the action of the lungs and heart is sluggish, as in cases of partial suffocation, of collapse in cholera, pneumonia, and other illnesses, is very valuable, and has been the means of saving many lives. Its use in cases of cyanosis, gout, diabetes, &c., has also been found advantageous. Wounds and sores are said to heal more rapidly in an atmosphere of oxygen than in air, and it has been largely used in this connection.

Methods of testing and estimation.—The readiest test is the property possessed by oxygen of moderate purity of re-kindling a glowing splint of wood, a property only possessed by one other gas—viz. nitrous oxide. A mixture of air and oxygen containing less than 30 p.c. by volume of oxygen does not ignite a glowing splint. When mixed with colourless nitric oxide gas, oxygen produces deep reddish-brown fumes of nitric peroxide, whilst nitrous oxide does not. Nitrous oxide is also much more soluble in water than oxygen. Ferrous sulphate and catechol mixed in an alkaline solution rapidly absorb oxygen and with the production of a deep red colour.

White indigo absorbs oxygen rapidly, at the same time turning blue. For general purposes of estimation, however, one of the three following methods is generally used:—

1. A solution of cuprous chloride in hydrochloric acid (which is colourless) absorbs oxygen readily with formation of cupric oxy-chloride. The greenish-brown solution of this salt may be again reduced by keeping copper foil in it.

2. An alkaline solution of pyrogallol absorbs oxygen freely, forming a dark-brown liquid. Carbon monoxide is evolved from the solution if the sodium hydroxide solution has a sp.gr. of less than 1·3; all sodium pyrogall oxide solutions evolve carbon monoxide if the oxygen content is more than 95 p.c. A reagent which evolves the minimum quantity of carbon monoxide is made by dissolving sodium hydroxide in its own weight of water and adding 5 parts of this solution to 2 parts of a solution containing 1 gram of pyrogallol in 3 c.c. of water (Jones and Meighan, J. Ind. Eng. Chem. 1919, 11, 311). Good results are obtained by mixing 45 c.c. of a 25 p.c. solution of pyrogallol (prepared by dissolving 60 grms. in 180 c.c. water) with 145 c.c. of 60 p.c. solution of caustic potash (prepared by dissolving 400 grms. ordinary stick potash in 300 c.c. water). 200 c.c. of this solution will absorb nearly two litres of oxygen, but it is better not to push the absorption beyond about 450 c.c. as then more or less carbon monoxide may be formed. Carbon monoxide is also sometimes formed when the percentage of oxygen in the gas being tested exceeds about 30 p.c. Clowes (J. Soc. Chem.

Ind. 15, 170, 742) recommends the use of a very large excess of potash to prevent the formation of carbon monoxide. He advises 160 grms. potash dissolved in 130 c.c. water, and 10 grms. pyrogallol added to the alkaline liquid. According to Hoffmann (Z. angew. Chem. 1922, 35, 325), the best proportion is 20 parts pyrogallol, 20 parts potash, and 60 parts water, or 40 grms. pyrogallol in 90 c.c. of water with 70 grms. of potash solution of sp.gr. 1·55. A still more active absorbent is made by suspending 11·4 grms. of powdered hydroxyquinol triacetate (prepared by the action of acetic anhydride on *p*-benzoquinone) in 20 c.c. of water, shaken in a hydrogen atmosphere with a concentrated alkali hydroxide containing 17·4 grms. of KOH, or the equivalent (6 mols.) of NaOH, diluted with 130 c.c. of water (Henrich, Ber. 1915, 48. 2006).

3. Clean moist copper absorbs oxygen freely, but a skin of sub-oxide is rapidly formed over the copper, which prevents further oxidation. An ammoniacal solution of ammonium carbonate, however, readily dissolves this sub-oxide again, leaving the clean copper. To utilise this reaction for analysis a suitable absorption vessel is packed with fine copper wire and then filled with a solution composed of equal volumes of ammonia of sp.gr. 0·930, and of a saturated solution of commercial ammonium carbonate. When the gas in which the oxygen is to be estimated is introduced into the vessel and displaces the liquid, a large surface of clean copper is exposed, and the oxygen is rapidly absorbed. When the residual gas is removed, the liquid again fills the vessel and dissolves the sub-oxide of copper formed, leaving the copper clean for the next analysis. 200 c.c. of this solution will dissolve the oxide formed by the absorption of about 4 litres of oxygen, but it is advisable to renew it after the absorption of about 3 litres, as otherwise a good deal of a yellowish-brown precipitate (probably an ammonia-copper compound) forms which renders the renewal more troublesome. A little fresh copper wire must be occasionally added as that in the vessel gets used up.

For all these tests Hempel's, Orsat's, or Stead's apparatus (*see* ANALYSIS) answers well for all but the most delicate determinations. With these an oxygen determination can easily be made in 10 mins.

If the first method is employed, the gas after absorption must be freed from hydrochloric acid by means of potash.

The property of phosphorus of absorbing oxygen at ordinary temperatures is also sometimes used for analytical purposes, but this is not a generally convenient method. A hydrochloric acid solution of chromous chloride or an alkaline solution of ferrous tartrate may also be employed.

Sheaff (J. Biol. Chem. 1922, 52, 35) describes a method in which small amounts of air or other gas containing oxygen are diluted with hydrogen and treated with excess of nitric oxide in presence of NaHO solution, and the resulting nitrite estimated colorimetrically by sulphanilic acid and α-naphthylamine in acetic acid solution, and comparison with a standard solution of sodium nitrite. Quantities of oxygen or the order of 0·1 c.mm., approximating to a weight of 1×10^{-7} grms. may be estimated with a maximum error of 4 p.c.

Applications of oxygen.—Oxygen has been used successfully to maintain the air in a respirable condition in places where it cannot be replaced, as in diving-bells, submarine vessels, &c. Its use has often been suggested in connection with the ventilation of large halls, theatres, &c., but the cost has hitherto proved too great for its adoption.

It is employed in conjunction with hydrogen or coal-gas to produce the oxy-hydrogen and oxy-coal-gas flames in which platinum can be melted, silver distilled, &c. One application of these flames is in the production of the Drummond or lime-light where the intense heat of the flame is made use of to raise a lime cylinder to a white heat and thus obtain an intensely vivid light. The oxy-hydrogen and oxy-coal-gas or acetylene blowpipe is also used for the brazing of metals, autogenous soldering, the blowing and manipulation of hard-glass apparatus, and for many other purposes where very high temperatures and local heating are required (*v.* also *infra*).

Oxygen is used for many purposes in the laboratory, and, as already mentioned, for some medical purposes. It has been found that the admixture of small proportions (up to 6 or 7 p.c.) of oxygen with nitrous oxide during anæsthetising with that substance prevents or reduces the tendency to convulsions experienced with pure nitrous oxide, without reducing appreciably its anæsthetic power. Johnson has shown (J. pr. Chem. [i.] 49, 148) that anæsthesia may be produced with nitrogen equally as well as with nitrous oxide, and that a mixture of nitrogen with 5–7 p.c. oxygen forms a very satisfactory anæsthetic, producing slight or no convulsions.

Oxygen has been applied in the purification of coal-gas from sulphur compounds. It is found that if from 0·5–1 p.c. of oxygen is added to the crude coal-gas before it enters the purifiers the reduction of the sulphur compounds to 8–12 grms. per 100 cubic feet of gas may be effected by lime alone, the use of oxide of iron or lime sulphide being unnecessary. If oxide of iron is used, its efficiency is increased. In any case the purifying space needed is lessened, the life of the purifying material is lengthened, and the luminosity of the purified gas is considerably increased. If lime is used for purification the fouled lime ('blue billy') has not the objectionable smell which it usually possesses (Valon, Trans. Gas. Inst. 1889, 41).

It has been found that if, during the bleaching of paper pulps and other materials with bleaching powder, oxygen in a fine state of division is introduced into the bleaching potcher, a great saving of bleaching powder is effected, the bleached fibre also being stronger in texture (Thorne, J. Soc. Chem. Ind. 1889, 83).

Pure oxygen is also advantageously employed in the oxidation and thickening of oils for varnish and linoleum purposes. The thickened oil is paler in colour than boiled oil, the danger is less, as only steam heat is needed, and the thickening, besides being much more rapid, is accompanied by increase of weight instead of by loss of weight as in the ordinary process of boiling. The use of driers is also unnecessary (Eng. Pat. 18628, 1889).

Oxygen is now sometimes used to hasten the maturing of spirits, the same effect being produced in a few hours or days by means of pure oxygen acting on the spirit in a finely divided state as occurs under the ordinary method of storage in casks in 2 or 3 years.

Proposals have been made to use a mixture of oil gas and oxygen as an illuminating gas (Tatham, Eng. Pats. 13763, 16138, and 16142, 1889). It was found that, if 15–30 p.c. of oxygen is added to an oil gas retorted at a low temperature from a heavy and crude petroleum, a gas of very high illuminating power and of good travelling properties is obtained. The gas is a perfectly safe gas, as about its own volume of oxygen must be added to a heavy oil gas before an explosive mixture is formed. The same inventor proposed (*l.c.*) to use carburetted oxygen as a motive gas for engines, &c. He claims that with properly constructed valves, &c., perfect safety is secured, and that the great expansive force of carburetted oxygen on ignition gives results far superior to those obtained in the ordinary steam or gas engine.

The use in the manufacture of vinegar of small quantities of oxygen to act as a stimulant on the mycoderma has been found to considerably increase the rate of acetification.

L. T. T.

The Production of Oxygen by the Liquefaction of Air.

Since 1902, the liquid air process for the production of oxygen has rapidly come to the front and with the single exception of the electrolytic method it is now the oxygen process almost exclusively employed for commercial purposes.

The separation of liquid air into its main constituents, oxygen and nitrogen, was a problem which for many years, prior to 1902, occupied the attention of physicists and chemists who have studied the practical production of extreme cold and the liquefaction of gases.

It was, however, not until 1895 that the first real step of importance was taken in the practical production of liquid air. In that year, Carl von Linde took out a patent (Eng. Pat. 12528, 1895) for an apparatus which marked a new era in the production of liquid air and probably the first serious step in the separation of its constituents.

It has been proved by Thomson (Lord Kelvin) and Joule that if compressed air were allowed to expand without doing external work there was a slight fall of temperature due to the fact that internal work must be done in such expansion. Linde first realised [1] that this cooling effect increased very rapidly as the temperature fell, and in his patent of 1895 he utilised the fact to make a most practical and effective air-liquefier. He took highly compressed air at ordinary atmospheric temperature and caused it to pass through a coiled copper pipe contained in a well-insulated heat interchanger, so constructed that the air which was allowed to expand through a throttle valve at the lower end of the coil was then caused to pass back in a reversed flow through the interchanger in intimate contact with the external surface of the pipe, through which the compressed air was passing on its way to the expansion valve. The principle of regenerative cooling was thus established between the expanded and compressed air with a self-intensive cooling effect which continued to increase until the cold became so great that a portion of the incoming compressed air was liquefied and collected in the vessel. Linde employed no preliminary cooling of the air, and by this simple construction of self-intensive counter-current interchanger, there is no doubt that he originated an air liquefying apparatus of much scientific value, although not perhaps of much direct commercial utility.

But in his 1895 patent, Linde did not aim merely at providing a simple method of producing liquid air; his real object was by liquefaction and subsequent fractional evaporation to separate its constituents in order to obtain oxygen of commercial purity. To do this, Linde relied on the fact that nitrogen being more volatile than oxygen the vapour from a liquid mixture of the two was richer in nitrogen than was the liquid itself. This process of fractional evaporation did not, however, prove successful. It was found by experiment that under the most favourable conditions in order to obtain a residue containing 50 p.c. of oxygen 70 p.c. of the liquid had to be evaporated, and that the further evaporation was carried the greater became the proportion of oxygen lost in the vapours. Thus in the end when the liquid approached the ordinary commercial standard of purity in oxygen its quantity had become so minute as to be practically valueless.

The following table, prepared by Linde from his own experiments, clearly shows how the composition of the liquid changes even under the most favourable conditions, viz. during slow or quiet evaporation:

Per cent. of liquid not yet evaporated	Per cent. of oxygen in liquid	Per cent. of oxygen in vapour coming off	Per cent. of original oxygen still in liquid
100·0	23·1	7·5	100·0
50·0	37·5	15·0	80·0
30·0	50·0	23·0	65·0
20·0	60·0	34·0	52·0
15·0	67·5	42·0	43·0
10·0	77·0	52·0	33·0
5·0	88·0	70·0	19·0

Between 1895 and 1902, many patents were taken out for the production of liquid air, and the separation of its constituents. Nearly all appear to derive their inspiration from Linde,

[1] It is a coincidence in the history of invention that the Eng. Pat. 10165 of 1895 was applied for by an Englishman, Dr. William Hampson, a few weeks before Professor Carl von Linde took out his British Patent. Hampson's patent is held by some to anticipate Linde in this country although there is no question as to the priority of Linde elsewhere. The terms of Hampson's provisional specification are somewhat ambiguous and it is difficult to say how much credit should be attached to this publication. Full details of Linde's apparatus were made known before the completion of Hampson's patent so that unfortunately his claim to priority has to stand on his provisional specification alone.

the low temperature for liquefaction of the air being obtained in practically every case by his nozzle expansion self-intensive system, whilst fractional evaporation of the liquid was invariably the system employed for obtaining oxygen.

As a matter of historical accuracy it must be admitted that for the seven years following Linde's patent of 1895 no substantial progress was made towards the industrial separation of oxygen from liquid air. It was not until 1902 (Eng. Pat. 14111, 1902) that Linde himself took the final step which solved that problem and laid the foundation for what is to-day undoubtedly the cheapest and best process for the production of oxygen.

It has already been shown that to obtain oxygen from liquid air by fractional evaporation a serious loss was entailed of the very substance that the process was designed to produce. It was this difficulty which Linde solved in his patent of 1902 and he accomplished it by adapting to the treatment of liquid air the process of rectification long known and employed in the production of alcohol (*see* ALCOHOL). Linde himself regarded his 1902 invention solely as an addition to the method of obtaining oxygen from liquid air by means of fractional evaporation as described in his 1895 patent, and he only claims it as such. By introducing a rectification column, however, on the top of his evaporation chamber he not only succeeded in arresting the oxygen which was formerly lost but actually employed it to form part of a continuous rectification process for the production of oxygen in a state of remarkable purity.

The simplest form of the Linde oxygen separator as employed to-day embodies all the essential features of his 1902 patent, so that a brief description of the actual machine with special reference to the accompanying diagrams may be taken as describing all the important characteristics of the apparatus as set forth in the specification and claim of that patent.

Fig. 1 represents diagrammatically the sectional elevation of a Linde separator capable of producing large quantities of oxygen of 98–99 p.c. purity. The circular upper portion of the casing, which is of wood, contains in its centre the rectifying column A, whilst the base constructed of wood in the form of a hexagon contains the vaporising, or distilling chamber B. All clearance spaces are packed with sheep's wool or other suitable insulating material in order to prevent the penetration of heat from outside sources. *c* is the counter-current interchanger constructed in the form of a large copper spiral pipe and containing three small copper pipes *d*, one of which is enclosed in a larger pipe *e*, as indicated more clearly in the sectional diagram, Fig. 2. c_1 is an extension of the main spiral pipe to the top of the rectifying column A with a gas or vapour collecting funnel F projecting within the same. e_1 is an open funnel-ended extension of the pipe *e* at the top of the vaporising chamber B. The pipe coil d_1, shown in the vaporising chamber, is connected at one extremity with the small pipes *d*, contained in the counter-current interchanger. The other extremity of this pipe is connected with the inlet of the valve G, to the outlet of which another pipe d_2 is connected as shown. This pipe is carried upwards and enters the rectification column near the top where it is fitted as shown with a rose end, the function of which will be explained later.

With this preliminary description of the essential parts the working of the apparatus can

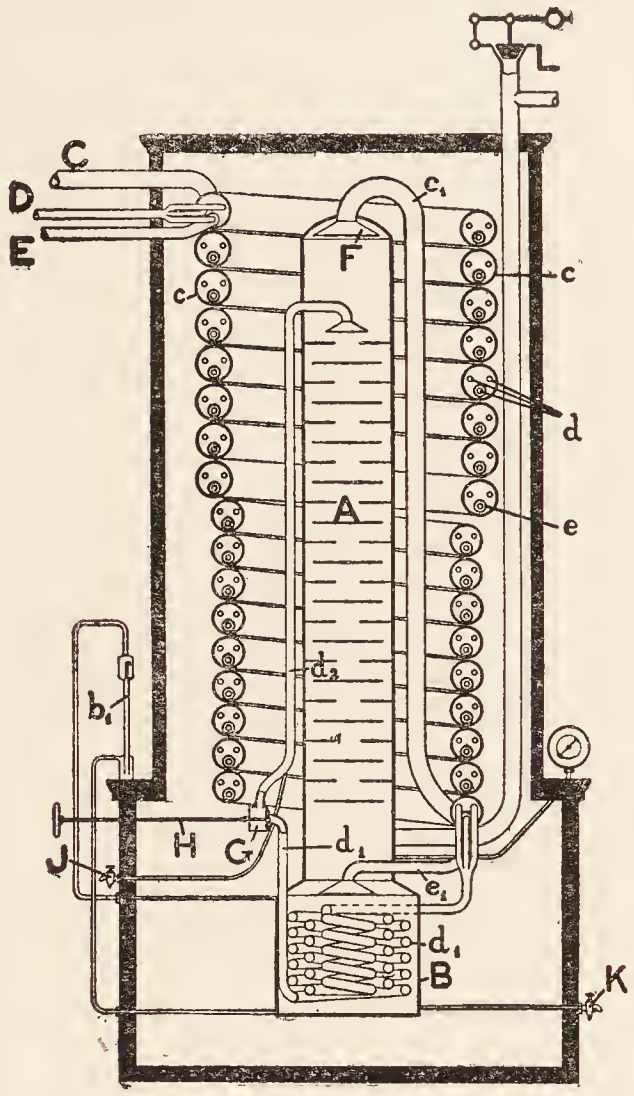


FIG. 1.

now be readily followed. There are two stages in the working. *First*, the preliminary cooling down and production of liquid, and *second*, the separation of oxygen from the liquid.

In commencing to work the machine, air at normal atmospheric temperature, or less, and at a pressure of about 2000 lbs. per sq. in. is conveyed from a gas compressor of suitable construction through the main pipe D, into the three small pipes *d* of the counter-current inter-changer. It passes down these pipes and through the pipe coil d_1 in the vaporiser to the inlet of the valve box G. At this point, by the adjustment of the regulating valve spindle H, the air is caused to expand from a high to a low pressure and is discharged at this low pressure through the rose ended pipe d_2 into the top of the rectification column. This expanded air fills the column and then flows through the only two possible outlets, c_1 and e_1, into the counter-current interchanger, in a reverse flow to the incoming high pressure air, leaving

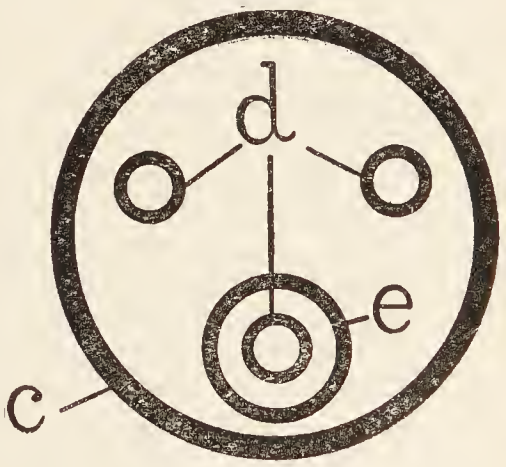


FIG. 2.

the apparatus through the pipes C and E as indicated.

It is at the valve G that Linde obtains the Thomson-Joule effect to which reference has already been made and regenerative cooling occurs in the counter-current interchanger where the incoming compressed air parts with some of its heat to the outgoing air which has been rendered colder by this temperature drop on expansion. The cooling effect throughout the whole apparatus goes on cumulatively until a temperature is ultimately reached at which the expanded air begins to liquefy and collect in that state round the coils in the vaporiser B. The quantity of liquid thus collecting is registered outside the apparatus by means of an ordinary coloured liquid which is contained in a glass tube b_1 enclosed in a pressure equalising circuit as indicated.

When the whole apparatus has been cooled down nearly to the temperature of liquid air, the liquid begins to accumulate rapidly in the vaporiser B, and the initial pressure of the air may be gradually reduced by increasing the opening of the valve G. Until this stage is reached, any separation of oxygen and nitrogen, which may have occurred, has been due simply to fractional evaporation.

As, however, the liquid begins to accumulate round the coil in the vaporiser B, the compressed air transmits some of its latent heat to the liquid. The latter is thereby evaporated whilst the compressed air is itself liquefied in proportion to the amount of heat thus extracted. The vapours thus produced begin to flow upwards through the rectification column in which the liquid air is flowing downwards. The temperature gradient necessary for efficient rectification then rapidly becomes established in the column and the second stage is reached in which the apparatus can be employed for the production of oxygen.

In the separation of oxygen from liquid air by rectification, Linde relies for his temperature gradient on the difference between the boiling-points of nitrogen and oxygen. The former is 77·5° absolute and the latter 91·5° absolute. Liquid air is discharged into the top of the column at a temperature of about 81° absolute. Nitrogen being the more volatile component it immediately begins to boil off, and thus automatically creates the maximum cold at the top of the column. For the same reason the nitrogen present in the original liquid collected in the vaporiser is the first element to be liberated by latent heat from the compressed air, so that the temperature of the liquid in the vaporiser becomes higher as its content of oxygen increases, thus the highest temperature is also established automatically at the bottom of the column. When all the nitrogen has been expelled from the vaporiser, liquid air passing down the column over various baffle plates comes into intimate contact with rising vapours of oxygen and an exchange of material takes place. At each stage some of the rising oxygen is condensed and some of the nitrogen in the downcoming liquid is evaporated whilst the liquid gradually gains in temperature until by the time it reaches the vaporiser its composition is that of practically pure oxygen. The gas, on the other hand, which passes off from the top of the column through the funnel F and the pipe c_1 to the counter-current interchanger, c, is mainly nitrogen at a temperature about 14° lower than that of the oxygen at the bottom of the column. The oxygen which rises in the column to effect the material exchange with the nitrogen of the liquid air is carried back to the vaporiser together with most of the oxygen contained in the original liquid. The excess of oxygen which thus continually gathers at the bottom of the apparatus is drawn off in a gaseous condition through the pipe e_1 into the pipe e of the counter-current interchanger. It will thus be seen that the gases drawn from the top and bottom of the apparatus are made to abstract heat completely from the incoming compressed air which is on its way to be liquefied.

The pressure at which the cold gases escape from the apparatus is from 4 to 5 lbs. per sq. in., just enough to cause them to pass freely through the counter-current interchanger. L is an emergency release valve on the low pressure system. J and K are test cocks communicating with the liquid air and liquid oxygen supplies respectively.

After the regular condition of oxygen producing has been reached the apparatus works steadily, the air supply from the compressor being kept at sufficient pressure not only to ensure its liquefaction at the temperature of the liquid oxygen bath (say 91° absolute), but also to ensure that the drop to the low pressure of from 4 to 5 lbs. sq. in. is sufficient to make good thermal losses due to leakage of heat from outside and to imperfect interchange in the counter-current apparatus. In practice, this pressure is found to be from 50 to 60 atmospheres.

A separate fore-cooler for the compressed air (not shown) is usually employed with the Linde apparatus. This fore-cooler is kept cold by means of a carbonic acid or an ammonia machine and is interposed between the air compressor and the separator so that the air leaving the compressor at normal atmospheric temperature becomes reduced to a temperature well below the freezing-point of water before it enters the separator. By this means, practically all the moisture which has not previously been abstracted by compression and chemical absorption gets frozen out of the air. This is a point of more importance in actual work than the slight supplementary cooling which is obtained, because unless the air is thoroughly dry before it enters the coils of the counter-current interchanger the working of the apparatus is liable to be interrupted by the formation of ice which has to be thawed out before work can be resumed. This is an operation which involves considerable delay. It is usual therefore to make both fore-coolers and separators in duplicate to ensure continuous working. In addition to the elimination of moisture it is also desirable to remove carbonic acid from the air. This is usually done by drawing the air on its way to the compressor through a purifier containing slaked lime. In practice, separators work for a week or longer without freezing up and fore-coolers for about two days.

The three essentials of Linde's process could not be more concisely or accurately described than in his own patent specification. They are

(1) cooling the air to be condensed in causing it to flow in the contrary direction to the evaporating products; (2) in then causing the same to transmit its latent heat to the evaporating liquid, and (3) in then causing the vapours produced in the distilling apparatus to flow upwards through the liquid flowing downwards in a stratified manner.

The first condition established the economy of the process by using the cold separated gases passing out of the apparatus to abstract heat from the incoming compressed air. It was by realising the possibilities of the second condition that Linde was able to achieve perfect rectification. Although the already cold compressed air is made to part with its latent heat while liquefying in the coils of the distilling apparatus its actual temperature cannot exceed that of the oxygen vapour which it has produced. By taking this liquid to the top of the column and letting it escape from a high to a low pressure the portion thus escaping undergoes an instantaneous partial volatilisation which, as already explained, reduces it so much in temperature that it can play the part of the cold member of the combination and thus establish the correct temperature gradient for the material exchange between liquid and vapour which the third condition renders possible.

The action which takes place in Linde's rectification column can be readily understood by reference to Bayly's experiments on the 'Distillation of liquid air and the composition of the gaseous and liquid phases at constant pressure,' published in 1900 (Bayly, Phil. Mag. 1900, 49, 517). It has already been shown

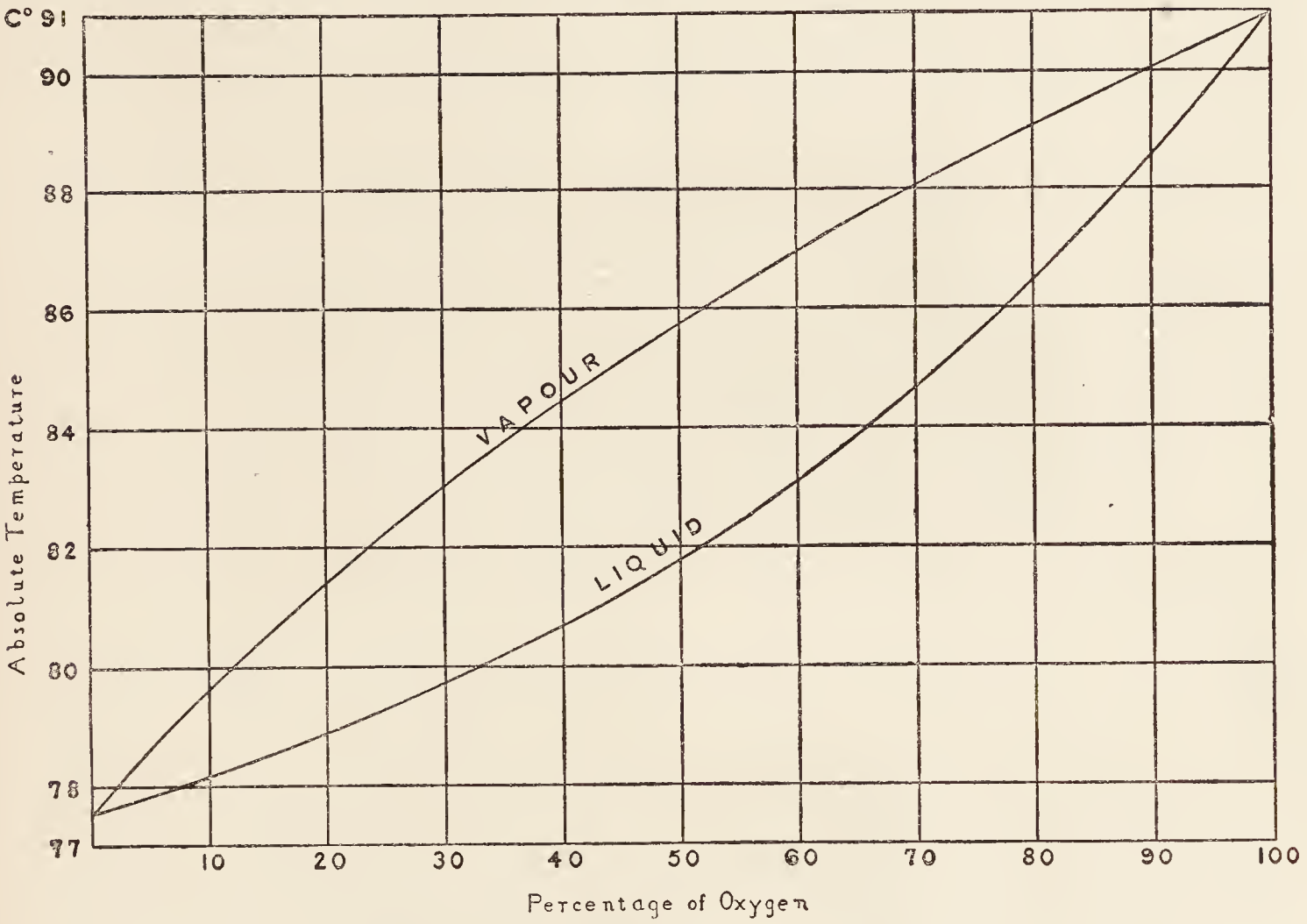


FIG. 3.

(table, p. 10) how the composition of the liquid air changes during slow evaporation. Bayly's experiments show that given any liquid mixture of oxygen and nitrogen equilibrium between its liquid and vapour is possible only where the vapour contains a definite proportion of the two constituents, but this proportion is not the same as that in the liquid.

The results in this direction obtained by Bayly in a series of experiments are graphically set out in the diagram, Fig. 3, in which the ordinates indicate temperatures and the abscissæ percentages of oxygen. The curves indicate the composition of liquid and vapour respectively at definite temperatures. From these curves it will be seen that with vapours and liquid in equilibrium the vapours are always richer in nitrogen than their liquid. Thus when the evaporating liquid is liquid air (oxygen 21 p.c., nitrogen 79 p.c.), the proportion of oxygen present in the vapour coming off must be not less than 7 p.c. Although it is therefore possible by simple rectification as employed in Linde's apparatus to expel all nitrogen from the liquid by material exchange with the oxygen vapours, nitrogen itself can never contain less than 7 p.c. of oxygen. Whilst, therefore, the apparatus is capable of producing—and does produce—pure oxygen it is impossible to obtain nitrogen of equal purity without further treatment (*see* NITROGEN).

With the correct temperature gradient of the Linde rectification column it is easy to apply the conditions of the Bayly curves. Starting with liquid air at the top of the column we know that 7 p.c. of oxygen must be present in the vapour given off. As the liquid descends it comes in contact with gas containing at each stage more oxygen than corresponds to conditions of equilibrium. Accordingly, oxygen is continually being condensed and nitrogen evaporated in the effort of the liquid to establish

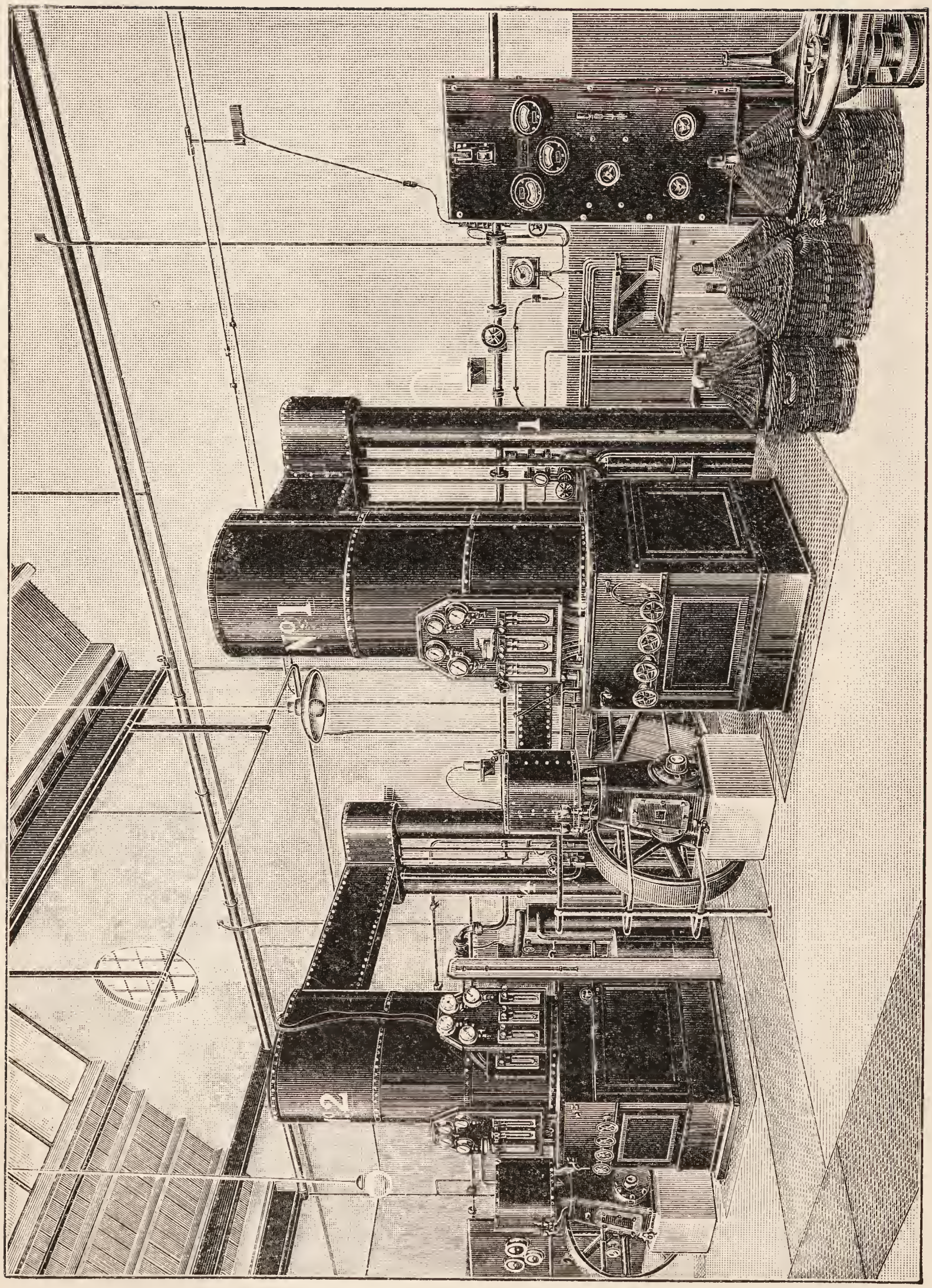


FIG. 4.—MANUFACTURE OF OXYGEN FROM LIQUID AIR. CLAUDE PROCESS (Wembley Works, British Oxygen Co.).
The illustration shows two Claude columns, each capable of producing 100,000 cubic feet of oxygen in 24 hours. The expansion engine is seen on the left of each column, and the interchangers are shown at the back.

a condition of equilibrium with a vapour of constantly changing partial pressures, until ultimately at the base of the column pure oxygen is obtained.

Rectification, according to Linde's invention of 1902, although it yields pure oxygen, cannot be regarded as complete because, as explained, it leaves not less than 7 p.c. of oxygen in the waste gas.

The rectification of liquid air has, however, undergone radical improvement in recent years, and to Georges Claude is due the credit of having produced what is undoubtedly to-day the most efficient apparatus for the extraction of oxygen and nitrogen from the atmosphere. Instead of condensing the compressed air integrally and then discharging it in one stream at the top of the rectifying column, Claude was the first to employ a fractional method of liquefaction which separates the air on condensation into two liquids, one containing an excess of oxygen and the other an excess of nitrogen. The liquid rich in nitrogen is discharged from the top of the column, whilst the liquid rich in oxygen enters the column at a lower point appropriate to the proportion it contains of the two components. The additional scrubbing thus obtained with a liquid richer in nitrogen than liquid air is the means of arresting a further 3 p.c. of oxygen without any additional expenditure of power. The waste gas consequently leaves the Claude apparatus with an oxygen content of only 4 p.c.

In the economical development of Linde's process Claude has effected further improvements. One of the most valuable of these is his method for utilising a considerable part of the energy contained in the compressed air by expanding it in a cylinder to perform external work. He thus obtains a greater degree of cooling than when Linde's system of nozzle expansion alone is employed, and he is able in consequence not only to work at much lower pressures but to dispense altogether with the fore-cooler which, as already explained, forms an integral part of the Linde apparatus.

Claude takes air from the compressor at normal temperature and at a pressure of from 20 to 35 atmospheres, according to the size of the plant employed. The compressed air then passes seriatim through two temperature exchangers (or counter-current interchangers), in the last of which the cold nitrogen and oxygen issuing from the separator are caused to abstract heat from the compressed air on its way to the separator. These temperature exchangers are thus used alternately as refrigerators, and are arranged to extract all moisture from the compressed air at the same time. The cold gases enter at the top of the exchanger in use and passing downwards through separate systems of small tubes yield their cold to the compressed air which rises upwards outside the tubes. The compressed air is thus as it ascends cooled down below the freezing point of water. Most of the water which it contains in a state of vapour falls to the bottom of the exchanger and is drawn off at intervals. A small residual is, however, gradually deposited in the form of ice round the tubes at the top of the exchanger. This necessitates the duplicate arrangement and alternate working of exchangers, for the one in use as a refrigerator gets gradually choked with ice. When this occurs the cold gases are turned into the other exchanger, and the compressed air is at the same time diverted so as to pass first through the exchanger which has to be thawed out. Thus each in turn acts as a refrigerator-drier for the compressed air, and thereby continuous working of the entire apparatus is assured. This arrangement has proved so efficient for drying the compressed air that the use of chemicals for supplementary drying is found quite unnecessary.

After passing through the temperature exchangers most of the compressed and cold air enters the cylinder of the expansion engine where its energy is absorbed in driving a dynamo or in doing other useful internal work, and from which it is discharged at a reduced pressure of 4 to 5 atmospheres and at a considerable reduced temperature. It then enters the lower compartment of a vaporising chamber at the bottom of the separator and is fractionally condensed by passing through a series of tubes, at the same time vaporising a corresponding quantity of liquid oxygen surrounding the tubes. The fractionated liquids fall into separate compartments from which they are forced into the rectifying column of the separator, as already described, in separate streams respectively rich in nitrogen and oxygen. These liquids descending the column as in the Linde apparatus, meet the rising vapours of oxygen when the exchange of material takes place in the usual manner and thus completes the purification of the liquid. The liquid discharged at the top of the Claude column being rich in nitrogen produces greater cold than is obtainable with the simple Linde column, consequently, the temperature gradient within the column extends lower, and thus ensures the more perfect abstraction of oxygen from the nitrogen, to which reference has already been made.

It was previously stated that most of the compressed air entered the expansion engine. The remainder of the compressed air is taken direct from the last exchanger (*i.e.* the one acting as the refrigerator-drier) through a small counter-current interchanger termed the liquefier, where it meets the very cold oxygen and nitrogen vapours issuing from the separator on their way to the exchanger. Here, as the name implies, a portion of the cold compressed air is liquefied by the Linde nozzle expansion method. This liquid enters the liquid chamber at the bottom of the vaporiser with the cold air issuing from the expansion engine. The liquefier thus serves the double purpose of maintaining the requisite quantity of liquid to make good all losses due to radiation or irregular working, and, as the flow through the nozzle is capable of adjustment, the supply of compressed air to the expansion engine can be diverted at will so that conditions of extreme cold in the expansion engine can be prevented. This is important, for, should the temperature of the gaseous air released from the expansion engine approach that of the liquid, its expansibility is reduced to an extent which renders the engine of little value as a refrigerating machine.

The Linde British patents were acquired in 1906 by the British Oxygen Company, Ltd., a concern which was founded as Brins Oxygen

Company, Ltd., in 1886 (*v. infra*). From the end of 1907 until March, 1909, the Linde rectification patent was the subject of long and important litigation which resulted in it being unanimously upheld both in the Court of Appeal and the House of Lords.

The British Oxygen Company possess oxygen factories in London (2), Birmingham, Wolverhampton, Coventry, Cardiff, Manchester, Birkenhead, Liverpool, Sheffield, Leeds, Newcastle-on-Tyne, and Glasgow. These, with two exceptions, are exclusively equipped with liquid air plant. Of the two exceptions one is equipped with both liquid air and electrolytic plants and the other with electrolytic plant only. The total capacity of all the Company's oxygen plants at the present time (1922) is upwards of 2,000,000 cub. ft. per day of 24 hours, the quality of oxygen being between 98 and 99 p.c.

The cost of production by the liquid air process varies considerably with the size of the plant. A plant to produce 40,000 cub. ft. of oxygen per 24 hours (which is a small size at the present time for a single unit in an oxygen factory) involves, in power, a total expenditure of about 100 b.h.p. Taking this at 0·35*d.* per b.h.p. hour, and adding all other direct charges, except depreciation and interest on capital, the cost per 1000 cub. ft. of oxygen into the holder works out at about 3*s.* 6*d.* The cost of such a plant complete with motive power, gas holder, and erection is approximately £8500. With larger plant units the cost of production and the capital outlay would appreciably diminish in proportion to this size.

The Production of Oxygen by the Electrolysis of Water.

With the steady reduction in the cost of electrical power which has taken place in recent years combined with improvements in electrolytic apparatus, the production of oxygen and hydrogen from water by electrolysis has undoubtedly been established on a commercial basis.

Of the various processes employed to-day, the best known are probably those of Garuti, Schuckert, and Schmidt.

In all apparatus for the electrolysis of water, two essential conditions have to be observed:—

First: Reduction to a minimum of the electrical power required.

Second: Perfect separation of the two gases.

Water itself, as an electrolyte, is a poor conductor. It is usual therefore in all cases to render the liquid alkaline by the addition of 15 p.c. caustic soda or 20 p.c. caustic potash in order to improve its conductivity and thus facilitate decomposition. Both the alkali and the water must be free from impurities, as otherwise irregularities occur in the working of the plant.

Efficient separation of the two gases depends largely on the construction and arrangement of the electrodes and diaphragms, or partitions, employed in the voltmeters, or electrolysers, as they are more commonly termed, and it is principally in this respect that the various forms differ. Where diaphragms are employed, they should be permeable to the electrolytic solution, impermeable to the gases evolved, and they should be good conductors. Many porous materials, such as porcelain, pipe-clay, asbestos, plates of carbon, &c., have been employed, but all appear to have failed to realise satisfactorily one or the other of the requisites mentioned.

The objection at first to the use of metallic diaphragms was that they came under the influence of the electric current by induction from the electrodes. They thus acted to some extent as bi-pole electrodes, thereby creating a tendency for the two gases to be liberated in the same compartment, or cell.

Garuti discovered that if the electromotive force did not exceed 3 volts, and if the current was under 2 amperes per square decimeter of electrode, a metallic diaphragm remained passive, and he found that owing to its feeble resistance it was possible to work the apparatus with a difference of potential well under 3 volts. Garuti discovered, however, that it was necessary to carry the bottom of the diaphragm below the level of the bottom of the electrodes in the electrolyser in order to ensure this passive condition, and that this construction prevented good circulation of the electrolyte. He overcame the difficulty by perforating a large number of minute holes in the lower or immersed portion of the diaphragm. Whilst these holes permit the electrolyte to circulate they are practically impermeable to the gases.

Figs. 4 and 5 illustrate diagrammatically a side elevation and cross section through AA of

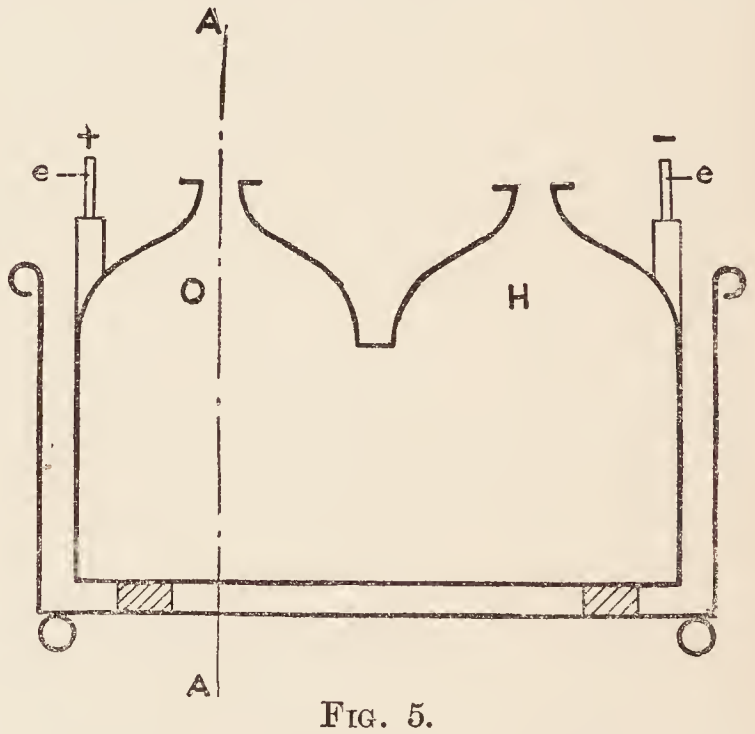


Fig. 5.

a Garuti electrolyser of this description. The outer tank in each is shown cut away.

The apparatus is composed of a series of alternate sheet steel compartments, or cells, *a b*, each enclosing an electrode *c* and consisting of long diaphragms *d* welded on to end plates and built up side by side. They are completely open at the bottom, and the lower portion of the diaphragm is perforated as indicated. They are all open at the top for half their length, those containing an anode, or positive electrode (viz. *a*), being open to the left half of the figure and those containing a cathode, or negative electrode (viz. *b*), to the right half of the figure. In this way the collecting bell or cover welded

on to the left portion o collects oxygen from the cells *a*, whilst the corresponding bell welded on to right portion h collects hydrogen from the cells *b*.

The anodes on one side and the cathodes on the other are welded to terminals *e* for the trans-

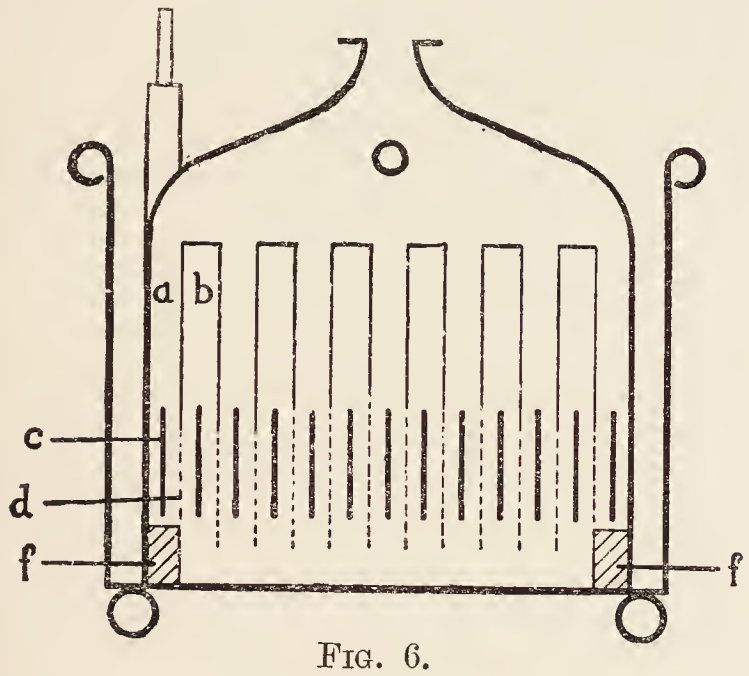


Fig. 6.

mission inwards and outwards of the current. When the electrolysers are large the diaphragms and the electrodes are maintained rigid and equidistant by means of wooden partitions, or combs *f* placed at the lower extremity as indicated.

In the Schuckert electrolyser, the separation is effected with the aid of a metallic partition, or screen, between the electrodes, each of the latter being metallically suspended from the centre of a gas collecting bell which seats itself in the electrolyte so that the gas liberated round each electrode can be separately collected. The screen which is insulated from the metallic bells is carried into the electrolyte so far below the edges of the bells, containing the anodes and cathodes, that the metallic surface of the bells is practically unaffected by the current lines set up in the electrolyte. On the other hand, the bottom edge of each electrode is carried so far below the bottom edge of the screen that the gases generated at the respective electrodes can be obtained in a pure condition. The bells containing the electrodes and also the screens are independently constructed and may be multiplied in one electrolyser as desired.

Both the foregoing types of electrolysers, which indicate the general construction of such apparatus, work without any special supervision. They are usually made to produce from one half to two cubic metres of oxygen per hour and consequently twice that quantity of hydrogen. The electrolysers are placed in batteries side by side in a room which must be provided with excellent ventilation, or a ventilating fan, chiefly in order to obviate all risks through leakage, of explosive mixtures of the gases. In order to attain its full capacity the temperature of the electrolyte should be from 50° to 60°. The temperature of the room containing the electrolysers is therefore apt to become excessive unless adequate ventilation is produced. The requisite heat is generated and maintained in the electrolyte by its own decomposition, but steam heating is frequently provided and particularly when the electrolytic apparatus is arranged to work intermittently.

The gases produced under normal working conditions in a good electrolyser have the following degree of purity :—

Oxygen, 96–97 p.c.
Hydrogen, 98–99 p.c.

The impurities are mainly oxygen and hydrogen respectively, and these residuals are largely eliminated by passing the gases through tubes containing heated palladium pumice on their way from the electrolysers to their respective holders. In the heated tube, the impurity in each case combines with some of the major gas in the form of steam, which is removed by condensation.

The first cost of a Schuckert electrolyser to produce ½ cubic metre of oxygen and 1 cubic metre of hydrogen per hour is given as about £75. Consequently for a plant to produce, about 40,000 cubic feet of oxygen per 24 hours, the electrolytic apparatus alone, assuming current to be taken from an existing private source, or public supply, exceeds the cost of a liquid air plant of the same capacity *with power included*. If the first cost of the current generating plant be added to that of the electrolysers it is probable that the complete electrolytic installation costs more than double that of liquid air. It should, however, be pointed out that in smaller plants this difference in first cost is not so marked, whilst hydrogen, as the electrolytic by-product, is at present a more useful commodity than the nitrogen of liquid air.

The cost of decomposing water by electrolysis into its components, oxygen and hydrogen, is mainly a question of the electromotive force involved, and the consumption of energy under normal conditions can be readily calculated from existing data :—

One ampere decomposes 0·335664 grm. of water per hour, and liberates 0·037273 grm. of hydrogen and 0·29839 grm. of oxygen.

One litre of hydrogen weighs 0·0896 grm.

One litre of oxygen weighs 1·4300 grms.

Therefore in one hour an ampere liberates from water 0·416 litre hydrogen and 0·208 litre oxygen.

Calculated on Thomson's law, according to which the heat disengaged by the formation of water equals the E.M.F. necessary for its decomposition, it is found that 1·5 volts is the E.M.F. required. In practice, it is not possible to realise this theoretical result and it is admitted that an E.M.F. of not less than 2·5 volts is necessary.

The production of 208 litres of oxygen, calculated on this latter voltage, gives $\frac{0{\cdot}208 \times 1000}{2{\cdot}5} = 83{\cdot}2$ litres of oxygen per kilowatt hour. Therefore, to obtain 1 cubic metre of oxygen and 2 cubic metres of hydrogen exactly, 12·0 *kilowatt hours are required.*

Schuckert gives the consumption of energy with his electrolytic system as 12 to 14 kilowatt hours per cubic metre of oxygen. The manager of a large factory in Germany, employing Garuti's process, recently gave the present writer the figure of 13·5 kilowatt hours as his experience, and 15 kilowatt hours has been given to the writer by other users of large electrolytic plant.

An average of 14 kilowatt hours (say) 20 B.H.P. hours, is consequently a reasonable estimate of power required in actual experience with large plants for the electrolytic production of one cubic metre of oxygen and two cubic metres of hydrogen.

An electrolytic plant of the capacity which has been considered in the case of liquid air, viz. an ouptut of 40,000 cubic feet of oxygen per 24 hours, requires therefore about 9 times as much motive power as the corresponding liquid air plant. Assuming that current is drawn from a public supply at $\frac{1}{2}d.$ per unit (a price at which it can be readily obtained to-day in many places), the cost of energy per 1000 cubic feet of oxygen is 16*s.* 8*d.* Allowing 2*s.* 4*d.* to cover other direct charges, such as wages, material, current losses, renewal of plates, &c., and assuming the same depreciation and interest on capital, then regarded as oxygen producing processes, the respective figures of 3*s.* 6*d.* and 19*s.* may be taken as a fairly accurate comparison of the cost of production.

It is obvious, therefore that unless a ready market can be found for hydrogen, the electrolytic process cannot at present compete on equal terms with liquid air plants in the oxygen factory.

Industrial Production and Uses of Oxygen.

Prior to Linde's invention of 1902, oxygen for industrial purposes was produced by electrolysis, except in this country where the Barium Oxide process was for many years successfully employed by the British Oxygen Company. The Barium Oxide process must to-day be regarded as obsolete because, in first cost, quality of oxygen produced and cost of production it is quite unable to compete with the liquid air process.

The electrolytic process, on the other hand, can at least supply a gas of equal purity, and where a useful outlet can be found for hydrogen the process is an admirable one for the production of oxygen.

Three circumstances have, however, conspired in recent years to arrest development in the use of electrolytic apparatus in the oxygen factory. The first is the established success of the liquid air process. The second is the introduction of oxy-acetylene welding which has not only largely superseded the older method of oxy-hydrogen welding but has in consequence created an extensive demand for oxygen, *per se*, thus detracting largely from the value of hydrogen in cylinders on which the success of the electrolytic process mainly depends. The third is the low price at which oxygen produced by the liquid air process can now be obtained in cylinders. This tends to restrict the sale of apparatus for private manufacture of the gas.

Undoubtedly the two most important industrial outlets for oxygen at present are oxy-acetylene welding and oxygen metal-cutting. Both processes are largely employed by engineers for an immense variety of metallurgical operations. The oxygen metal-cutter is probably the most remarkable labour-saving tool that has ever been introduced, and it is no exaggeration to say that 60 p.c. of the oxygen used at the present time is employed for cutting.

The demand for oxygen due to the development of welding and metal-cutting has led to the erection of many oxygen factories in recent years all over the world.

In this country the supply is at present almost exclusively in the hands of the British Oxygen Company. That company now distributes in cylinders from its various factories upwards of 250,000,000 cubic feet annually. In Francc the output is at least equal to that amount, and in the United States of America and Germany it is probably largely exceeded. The price of oxygen varies from $\frac{1}{4}d.$ to $\frac{1}{2}d.$ per cubic foot, according to the locality and the quantity purchased.

Oxy-acetylene welding.—The temperature of the flame in a good oxy-acetylene blowpipe is approximately 3315° (6000°F.). This high temperature is mainly brought about by the combustion of carbon to carbon dioxide. Acetylene has a heating value of about 1500 B.T.U. per cubic foot. It is an endothermic gas approximately composed of 92·5 p.c. carbon and 7·5 p.c. hydrogen, which in combustion with oxygen form carbon dioxide and water. In consequence of the high flame temperature, however, the water formed by this primary combustion is dissociated into hydrogen and oxygen, the latter element combines at once in the flame with the carbon of the acetylene to form carbon dioxide, whilst the hydrogen can only combine with oxygen which has passed out of the hottest zone of the flame, and thus does not involve a consumption of heat at the expense of the hottest part. It is, in fact, claimed for oxy-acetylene welding that the hydrogen forms a relatively cool jacket round the hot flame produced by the combustion of carbon in oxygen, and that as the hydrogen is not able to combine with oxygen at the very high temperature which exists within the inner zone, but remains temporarily in a free state, it protects the inner zone in a measure from loss of heat, whilst largely excluding the tendency to oxidation of the metal—a defect from which all other methods of welding suffer.

Theoretically, $2\frac{1}{2}$ volumes of oxygen are required for the complete combustion of 1 volume of acetylene. In practice, however, with the oxy-acetylene blowpipe, it is found that the best welding results are obtained with 1·25 volumes of oxygen to 1 volume of acetylene.

The strength of the weld produced by the flame is almost invariably somewhat less than that of the original material. This may often be due to the use of welding strips of inferior tensile strength. It is, however, undeniable that the structure of the material in the weld is less homogeneous than in other parts. A good weld is largely a matter of skill on the part of the individual welder. It is possible for a competent welder, at his own discretion, to give a greater or less strength to the welded part, and for this reason it is impossible to draw conclusions from the work of one man as to the work of another. Oxy-acetylene welding must be regarded as a trade which can only be mastered by intelligent work and gradual development from simple to difficult jobs. Much depends on the intelligence and ability of the workman. A skilful welder will use a hammer freely as well as a blowpipe, more

especially on vertical or overhead welds in plates which are subsequently to be subjected to pressure strains. By the judicious use of hammering at the right moment on the welded part the metal can always be made denser, with the result that the strength of the weld is increased.

The oxy-acetylene system of blowpipe welding is employed in two forms, which may be described as the high and low pressure systems.

The first to be introduced was the high-pressure system, in which both gases are delivered to the blowpipe under pressure. Oxygen is supplied from an ordinary trade cylinder, and acetylene from a cylinder in which it is dissolved in a porous material soaked in acetone. Acetone has the property of absorbing 25 times its own volume of acetylene at atmospheric pressure, and it continues to do this for every atmosphere of pressure that is applied to the gas. This system affords an excellent and safe method of transporting acetylene and it supplies engineers with the means of using the oxy-acetylene blowpipe in its most portable form. It has many useful applications, and for repair work generally, but more especially on board ship, this system is admirably adapted.

The low-pressure system is almost exclusively employed for welding purposes in engineering works. In this latter method, only oxygen is required from a cylinder. Acetylene may be taken from any ordinary generator of approved design.

Oxygen has to be supplied to the blowpipes at a constant low pressure of from 5 to 30 lbs. according to the size of the blowpipe employed. For this purpose the high and varying pressure of the gas cylinder is reduced to the constant low pressure required, by means of a pressure regulator which is attached to the cylinder. Acetylene (which must be well purified) is conveyed by any suitable system of piping from the holder of the generator to the place where it is to be employed. The blowpipes used are invariably of the injector type in which the oxygen under a suitable pressure is made to draw the necessary quantity of acetylene into the blowpipe and then deliver both gases well mixed and under sufficient pressure through the burner nozzle.

Fig. 6 illustrates a popular type of an injector blowpipe which, in addition to possessing all the usual characteristics of such a tool,

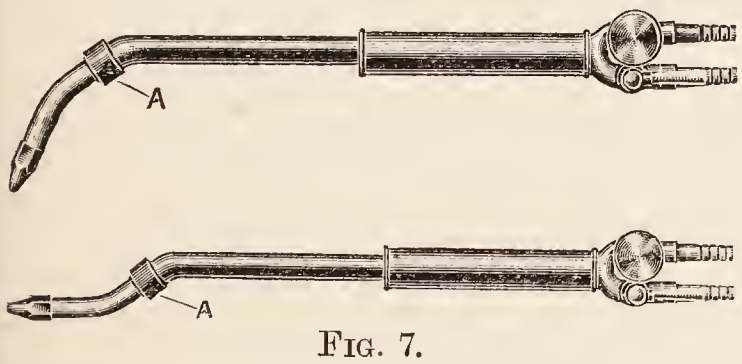


Fig. 7.

s fitted with a head which can be adjusted as indicated to suit any special conditions of work.

It is impossible to enumerate in detail all the work which may be executed by the oxy-acetylene blowpipe rapidly and economically, but the following are some of the applications for which it has already been advantageously employed :

The fusion welding of bicycle frames, forks, tee standards, wheel rims, &c. ; the fusion welding of frames, wheel rims, &c., for motor cars ; the repair of locomotive frames, &c. ; in the manufacture of iron or steel motor or other boats as a substitute for rivets ; the fusion welding of domestic and other hot-water boilers ; the repair of steam boilers, boiler flues and other apparatus *in situ* ; the fusion welding of steel or iron tanks, &c. ; in the manufacture of safes ; the fusion jointing of pipes of every description and shape for steam superheaters, &c. ; the fusion welding of all joints in metallic casks, petroleum barrels, &c. ; as a substitute for riveting in thin sheet ironwork, such as enamel ware ; artistic ironwork ; the repair of cracks, blisters, and flaws in iron and steel castings, forgings, &c. ; as a substitute for brazing in many instances.

Metal cutting by oxygen.—This process is based on the well-known fact that a jet of oxygen directed upon a previously heated spot of metal ignites it, with the result that the metal acting as its own fuel burns away rapidly in the form of metallic oxide.

In the year 1889, the late Mr. Thomas Fletcher, of Warrington, showed that, after heating an iron plate to incandescence by means of the oxygen and coal-gas flame obtained with one of his blowpipes, it was possible, by largely increasing the supply of oxygen, to ' fuse ' holes and even slots in the plate.

Twelve years later, the same process was applied practically by Dr. Menne, of Germany, to the opening up of tuyeres in blast furnaces which had become blocked by the solidification of metal.

The use of oxygen for this latter purpose proved so successful that its value in the cutting of metal was again suggested. Theoretically, once iron is ignited in oxygen, if a powerful jet of the gas is maintained in operation, it should be possible to burn away the metal without any auxiliary source of heat. Oxide of iron, however, is formed at a comparatively low temperature and lacks fluidity. It was found difficult in practice to eliminate all the oxide which was formed. Much of it adhered to the partially molten metal, thus preventing the intimate contact of metal and gas, with the result that combustion soon failed, and the cutting operation was arrested. The process was in consequence intermittent, the consumption of oxygen wasteful, and the cut wide, coarse, and irregular. In 1904, a cutting blowpipe, which is a very simple solution of this difficulty, was introduced by the Société Anonyme L'Oxhydrique Internationale of Belgium. It consists essentially of an oxy-hydrogen, oxy-coal-gas or oxy-acetylene blowpipe, with an additional passage through which an independent and separately controlled stream of oxygen is supplied at the discretion of the operator. This separate supply of oxygen may be discharged through the centre of the blowpipe, in which case the mixed gases employed for heating are conducted through an annulus surrounding it, or the supply may be brought in a passage immediately behind the heating flame.

This simple expedient of maintaining an independent heating jet in operation whilst the cutter is travelling renders the cutting operation continuous. It furnishes the quantity of additional heat necessary to render the oxide

fluid, so that it can be blown away through the cut by the separate jet of oxygen.

The cutting operation is very simple, and can be mastered by any intelligent workman in a few hours. The edge or surface of the plate at the point to be cut is first heated by the mixed jet of oxygen and any suitable fuel gas. When this spot has been brought to a state of incandescence, a fine cutting jet of oxygen is discharged upon it. This immediately produces combustion of the metal, with the resulting formation of iron oxide. The jet of oxygen is made sufficiently strong to blow away this iron oxide in front of it, with the result that a clean narrow cut is effected through the metal at a speed of travel which is comparable with hot sawing. The metal on each side of the cut is neither melted nor injured in any way, as the action proceeds too rapidly for the heat to spread; in fact the edges present the sharp and purely metallic surface of a saw cut.

The cutting may be made to follow any desired line, exccuting circles, curves, or profiles as desired, for which purpose guides and other mechanical contrivances are employed. Bevel cuts can be made and the process can be employed for the cutting of all grades or conditions of steel, as the action being chemical rather than mechanical the quality of the metal does not materially affect the results.

Fig. 7 illustrates a popular type of hand metal cutter, of the concentric type, in which

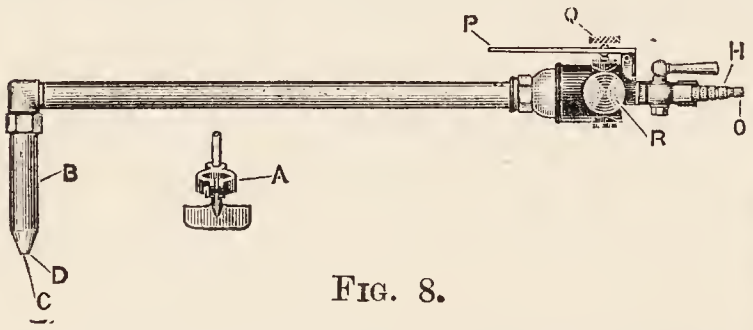


Fig. 8.

the oxygen for cutting is discharged through the centre of the blowpipe whilst the mixed gases for heating are conducted through an annular passage surrounding it, all gas supplies being separately controlled.

Special appliances are supplied for ensuring a steady movement of the hand cutter, a matter of considerable importance where neat and accurate work is desired. In fact, machines and appliances are constantly being devised with the object of extending the applications of the process and of improving the results obtained.

The process may be employed for cutting sections of any thickness up to and even exceeding 12 inches, and the same cutter can be employed without any structural alteration on plates varying in thickness within wide limits; all that is necessary is to increase the velocity and quantity of oxygen used for cutting, to correspond with the increased thickness of the plate.

As indicating the remarkable possibilities of this process, the following results obtaincd in the cutting of nickel-chrome steel armour plate are intercsting.

With a single jet of oxygen, a plate $9\frac{3}{4}$ in. thick was cut through at the rate of one foot in $3\frac{1}{2}$ minutes with a consumption of 30 cubic feet of oxygen per foot run.

A plate, 12 in. thick, was cut through at the rate of one foot in $4\frac{1}{2}$ minutes with a consumption of 50 cubic feet of oxygen per foot run.

Such results as these indicate the immense field of operation both in constructional and destructional ironwork which is covered by this important application of oxygen. K. S. M.

OXYHAEMOGLOBIN *v.* Blood.

OXYLIQUIT. Liquid air mixed with oxidisable substances, such as wood charcoal. Used as an explosive.

OXYLITH. Trade name for sodium peroxide.

OXYNARCOTINE *v.* Opium.

OXYPHENINE (*Chlorophenine, Chloramine Yellow, Diamine Fast Yellow B, 2 F, etc.*) *v.* Primuline and its derivatives.

OXYPHLOROGLUCINOL *v.* Phenol and its homologues.

OZOKERITE, known in Germany also as *Erdwachs, Bergtalg, Bergwachs, Fossileswachs, Mineralfett, mineralisches Leischenwachs*, in Moldau also as *Zietrescit*, and in the neighbourhood of the Caspian Sea as *Naphtgil, Naphatil, Neftgil, Neftegil, Neftachil*, is a naturally occurring solid hydrocarbon of the olefine, or C_nH_{2n} series. Ozokerite is found chiefly in the Miocene formation in Boryslaw, near Drohowycz, and in the region of Stanislawow, Poland. The veins in which it occurs are 40 to 80 mètres deep, and 1 mètre in thickness. They pass through beds of sand, from 8 to 10 mètres deep, containing large stones, and then through blue clay and a plastic loam. From this blue clay, naphtha usually springs. The centre of the basin is richest in wax; in some cases masses of such extent have been tapped that the miners have hardly had time to escape before the workings were filled with the plastic mineral. Such a deposit was found in the deepest shaft at Boryslaw, at a depth of 208 mètres (227 yards). In general, however, the yield of wax varies at from 4 to 8 p.c. of the mineral extracted. Ozokerite was discovered in 1833 by Dr. Mayer, in Slanic in Roumania, and Glocker, who analysed it in the same year, gave the mineral this name, deriving it from two Greek words meaning 'to smell' and 'wax.' It was discovered in Poland by Doms in 1854. At first it was regarded as an unwelcome companion to the petroleum, as it frequently caused the timbering of the shafts to collapse. It was not until about 20 years later that this substance began to attain commercial importance, a method having then been discovered of producing from it a substance resembling beeswax and named ceresin.

In 1865, ozokerite, which had previously been regarded as a Crown mineral, was declared free, and the consequence was that a number of shafts were sunk in the district, and much speculation ensued. The land being parcelled out in small plots, the shafts were sunk in the immediate neighbourhood of each other, and much waste and danger ensued. In 1886, a law was passed, whereby the right of mining for ozokerite might be separated from the ownership of the land. In 1899, it was further enacted that shafts were to be at least 60 mètres distant from one another. The extraction is now carried out under official supervision. In nearly every case the mineral is raised through vertical shafts or pits over which a wooden roof is erected. The section of the shafts in the first instance is 4 square mètres (43 square

feet); but, when the ozokerite formation is reached, an inner shaft 1 mètre square (10·76 square feet) is formed of timber, and the space between this and the timbering of the larger shaft is filled with a rich clay. This construction is adopted to exclude the surface-water, which is now kept down by machine-driven pumps during the sinking. From the bottom of the shafts levels are driven into the ozokerite ground, the richer portions being raised and the refuse used to fill up the old workings. The softer parts of the marl are dislodged by means of pick or wedge; but where the rock is hard, and the permission of the mining authorities can be obtained, dynamite is used. The mineral used to be raised by hand in skips or tubs holding 40 to 50 kilos. (88 to 110 lbs.). But electricity has now been applied to the haulage and this has greatly increased the output, two men now being able to raise 120 skips of 135 kilos. per day where four men were needed to raise 60 skips of 50 kilos. in the same time. Modern methods of ventilation and electric light have now mostly replaced the hand ventilators and safety lamps formerly employed. The timbering of the shafts requires constant renewal and repairs; in some cases it is almost impossible to keep the shafts perpendicular.

The water is usually raised in tubs, and much difficulty is experienced in getting rid of it after it reaches the surface, on account of the numerous shafts and the broken nature of the ground. Costly modern pumping stations and machines have now been erected for this purpose. The mineral, when it leaves the tubs, is sorted by hand. The waste rock is picked out and tipped to spoil, lumps of ozokerite are specially selected, and the remainder of the rock, containing fragments of wax, is tipped into banks full of water. On being well stirred, most of the wax rises to the surface and is skimmed off. The residue still contains from 2 to 3 p.c. of wax. A more costly, but more thorough, method of separating the wax is sometimes employed. The mineral, after being hand picked, is tipped into cast-iron vessels, and water at 50° is poured over it. The tanks are heated gradually from below, until the water boils. At 60°–70°, the melted wax which rises to the surface is ladled off and poured into cold water where it solidifies, after which it is removed and the water contained in its pores removed by pressure. A further quantity of wax is obtained by stirring the remaining hot contents of the tanks. This process is known as Lep-boiling (Lepkochen) (J. Soc. Chem. Ind. 1892, 117; *ibid.* 1898, 236; Eng. Pats. 2242, 1890; 9781, 1891; Die Zeresinindustrie, by Bela Lach, 1911). The quantity of waste mineral being considerable, and the distance between the shafts small, a special railway has been built to remove the residues from the immediate neighbourhood of the mines.

It has also been attempted to extract the wax by means of solvents such as benzene, but only with very poor results. The wax so obtained is of a much lighter colour and higher melting-point (73°) than the ordinary kinds, but is, nevertheless, not so useful in the ceresin industry.

The production of ozokerite in the Boryslaw district amounted, in 1887, to 96 p.c. of the total output in Poland, and was valued at £152,900 (J. Shotsky, Allg. österr. Chemiker- und Techniker-Zeit. 1889, 614, 651; J. Soc. Chem. Ind. 1890, 597; *ibid.* 1892, 117; *ibid.* 1897, 774).

Since the production of ozokerite has become more costly, its output has decreased. Thus in 1904, Poland, which practically supplies the whole world with the crude product, only produced 2908 tons.

The ozokerite forms lumps and layers from 3 to 9 decimètres thick, so that masses are often found about 100 kilos. in weight.

Other deposits of ozokerite are found at Truskawice, Starunia, Dwiniacz, Klecany, and Pruthale, always in Miocene formations.

It has also been found in Hungary by the river Iza in the neighbourhood of Pecora. Its quality here is similar to that in Poland. In various parts of Roumania, also, excellent ozokerite deposits exist.

Ozokerite is found in the Caucasus, and among the Wasatch Mountains, Utah, about 173 miles east of Salt Lake City, America, where deposits of white ozokerite, miles in length, are said to be found.

Caucasian ozokerite resembles an inferior Polish variety. Melting-point of crude substance 68°. Treated with 20 p.c. of fuming sulphuric acid it yields 58·1 p.c. of second-quality ceresin; m.p. 68·5°; volatile portion, 1·8 p.c. The crude substance has a repulsive odour, is worked with difficulty in quantity, becomes stiff in the basin, and presses extremely badly (Lach, J. Soc. Chem. Ind. 1885, 488).

Rich deposits of ozokerite have also been found along the banks of the Kemioki near Tornea (J. Soc. Chem. Ind. 1901, 1043) and in the Island of Chelekon in the Caspian Sea (*ibid.* 1896, 932).

North American or Colorado ozokerite.—Here extensive deposits of an ozokerite like substance are found, the supply from which is hindered only by the transport difficulty. On being tested, however, the material seems to be of little use for the production of ceresin. It is supplied in cakes $36 \times 20 \times 6$ cm. in dimensions. It is a dull black, hard substance, brittle and pulverisable, and smelling of catechu. Care must be taken in heating it, as violent frothing may occur from the presence of water.

The crude substance melts at 76·0°.

Treated by the above-mentioned process no ceresin is obtained. Even when heated to 300° it is impossible to filter it, although it is quite a thin fluid. Subjected to distillation it gives the following results:

	Per cent.
Paraffin oil	90·00
Gas	2·12
Water	2·60
Residue	5·28

It commences to distil at 360°, when nearly 3 p.c. of oil, solidifying at 30°, comes over. At a much higher temperature it distils steadily, giving a very fair crude product for paraffin extraction. This substance is apparently more suitable for paraffin-making than for the ceresin industry (B. Lach, J. Soc. Chem. Ind. 1889, 696).

In Utah, a dark brown ozokerite of m.p. 53°–55°, sp.gr. 0·9285, has been found (Seal, J. Franklin Inst. 1890. 100, 402; Parker, J. Soc. Chem. Ind. 1891, 736). A similar material

occurs at Thrall, Texas. It melts at 79·5°. The ceresin prepared from it melts at 75° and has sp.gr. 0·926–0·928 and refractive index 1·4414–1·4420 at 90°. Ozokerite is also found in Portuguese East Africa, in Ghazaland, and in many other parts of the world, but generally either in too small quantities or of too poor a quality to make its extraction on a large scale profitable.

Ozokerite varies in composition, in m.p. (56°–100°), in b.p. (210°–300°), and in sp.gr. (0·85°–0·97°), depending on its source. The native ozokerite is transparent, of a light yellow colour, and of the hardness of beeswax. It smells like benzene or petroleum, but the harder varieties are almost odourless. The best ozokerite is yellow or greenish, and can be easily compressed between the fingers. This kind, however, is not much used for the preparation of ceresin. Ozokerite consists chiefly of heavy saturated hydrocarbons, together with unsaturated hydrocarbons and other substances (Gosling, J. Soc. Chem. Ind. 1898, 741; Israti, Chem. Zentr. 1897, i. 1222; *ibid.* 1904, ii. 1448; Fader, *ibid.* 1905, i. 1666; Morozewicz, *ibid.* 1909, i. 1113). It appears to have been formed by the oxidation and decomposition of the hydrocarbons of naphtha, since the action of oxygen on these compounds simply eliminates hydrogen. Thus, for example, naphthalene gives dinaphthyl and water:

$$2C_{10}H_8+O=C_{20}H_{14}+H_2O$$

By further oxidation compounds are obtained of the formula C_nH_{2n}, which react with the hydrocarbons of the marsh-gas series, with formation of very complex carbon compounds of various melting-points, as for example:—

$$2C_8H_{18}+O_2=C_{16}H_{32}+2H_2O, \text{ and}$$
$$C_{16}H_{32}+C_8H_{18}+O=C_{24}H_{48}+H_2O$$

According to this hypothesis, the formation of ceresin from naphtha by the oxidation of the compounds of the marsh-gas series, and the relationships of ozokerite, naphtha, and coal, can be explained in the simplest manner (Gosling, *l.c.*; Engler, Chem. Zeit. 1906, 30, 711; Künkler and Schwedhelm, Chem. Zentr. 1908, i. 1322; Rakusin, J. Russ. Phys. Chem. Soc. 1909, 41, 109; *cf.* Marcusson and Schlüter, Chem. Zeit. 1914, 38, 73).

The best kinds of ozokerite are used in the preparation of ceresin. For this purpose, the crude ozokerite is broken into small pieces and melted in tanks by the aid of steam coils. The mass is run into retorts and distilled with steam. When the distillate has cooled to an oily mass it is subjected to hydraulic pressure, after which it is again melted and treated with fuming sulphuric acid in vessels fitted with stirrers. A full description and figures of the plant and materials employed are given by Lach in his Zeresinfabrikation, 1911; *v.* also Gosling (*l.c.*). A number of methods of purification are also described in this work (*v.* also Marcusson and Schlüter, Chem. Zeit. 1907, 31, 348).

Good ceresin is not easily distinguishable from beeswax. The following are the best methods of discrimination—(1) Ceresin is not so easily kneaded between the fingers as beeswax, and is more brittle. A mixture of the two bodies cannot be recognised in this way. (2) Ceresin is almost unacted on by concentrated sulphuric acid, whilst beeswax undergoes perfect decomposition by such treatment. To reduce its cost and also to render it harder and more wax-like, ceresin is often adulterated with paraffin, rosin or colophonium, petroleum oil, or with carnauba and Japan wax.

In addition to the production of ceresin, ozokerite is used in the manufacture of candles, ointments, pomades, and shoe blackings. It is also employed to some extent in the manufacture of shining black paper and for the impregnation of certain kinds of wood in furniture manufacture.

Under the name of *okonite*, the residue remaining after the purification of ozokerite forms an excellent insulating material for electric cables (J. Soc. Chem. Ind. 1905, 518) and with an admixture of 50 p.c. india-rubber, ozokerite is recommended as a very good insulating material.

Paraffin was formerly obtained from ozokerite by distilling the residue, forming ozokerite pitch.

Ozokerite vaseline is obtained by allowing melted ozokerite to pass through 12–30 filters of animal charcoal (depending on the degree of decolorisation required). The mass is then treated with superheated steam for 3–4 hours at 250° (Gosling, *l.c.*).

OZONE. Sym. O_3; molecular weight, 48. Van Marum, in 1785, noticed that air or oxygen in the neighbourhood of an electrical machine, or through which a series of electric sparks had been passed, acquired a peculiar odour, somewhat resembling that of chlorine; and Cruickshank, in 1801, noticed a similar smell during the electrolysis of water. But Schönbein, in 1840, was the first to recognise that this smell was due to the formation of a new gas, to which he gave the name ozone (ὄζω, I smell). Shortly afterwards he found that ozone was also formed by the action of moist air on phosphorus. At first this substance was considered to be an oxide of hydrogen, but the researches of Marignac and De la Rive, of Andrews and Tait, of Frémy and Becquerel, of Brodie, and others, and especially of Soret, established the fact that ozone is an allotropic form of oxygen produced by the condensation of three volumes of oxygen into two of ozone; or, in other words, that, whilst the molecule of oxygen contains two atoms, that of ozone contains three. Its formation may be expressed by the equation $3O_2=2O_3$. One view held for some time was that ordinary oxygen was composed of negative oxygen, or *ozone*, and positive oxygen, or *antozone*, but the existence of the third form, or *antozone*, has not been proved.

Preparation.—As already stated, ozone is formed when a series of electric sparks is passed through oxygen or air, but the proportion of the oxygen so transformed is very small. A much larger proportion of ozone is formed when the silent discharge is substituted for the spark discharge, a contraction of the volume of air or oxygen occurring at the same time.

For this purpose a current of air or oxygen is passed between the terminals of an induction coil placed at a short distance apart and made as large in area as possible. The original Siemens 'induction tube' (1857) consisted of two concentric glass tubes, the outer tube being covered, the inner lined, with tinfoil. A current of air or oxygen is passed through the

narrow annular space between the tubes, the metallic surfaces of the inner and outer tubes being connected with the terminals of an induction coil or electrical machine, and thus transformed into terminals of large area. A number of modifications of this apparatus have been employed. In some of these the metallic terminals are replaced by good conducting solutions, such as copper sulphate solution, &c., in others by shot, powdered graphite, &c., and the inner glass tube may be advantageously replaced by a metal tube. In many forms the terminals consist of flat metallic plates placed close together with a sheet of dielectric (glass, mica, &c.) between them, in others one or both poles consist of one or more points. Some inventors have claimed to get better results without the solid dielectric, relying only on the thin layer of air or oxygen between the plates as the dielectric. There is, however, little doubt that the solid dielectric between the electrodes is advantageous; on the one hand, acting as a condenser it increases the regularity of the discharge, and on the other, it very greatly reduces the tendency to sparking. But in all cases the principle is the same, viz. the passage of a current of air or oxygen between terminals of large area, placed very close together, and thus offering as little resistance as possible to the silent discharge and reducing sparking to a minimum.

More ozone is obtained when a current of oxygen is used than when air is employed. The proportion is also increased by thoroughly drying and cooling the oxygen, by increasing the pressure of the air or oxygen, and by bringing the terminals as near together as possible. Sparking is very detrimental, destroying much of the ozone formed. The best result is obtained when there is a continuous 'glow' discharge. If the air is moist, some nitric acid is almost invariably formed. Under favourable conditions, and when great care is taken to keep the temperature of the apparatus and gas low, about 25 p.c. of the oxygen may be converted into ozone; but ordinarily, or on the large scale, the proportion obtained is much smaller.

Briner and Durand (Compt. rend. 1907, 145, 1272), by immersing their ozoniser in liquid air at a temperature of −194° succeeded in converting 99 p.c. of the oxygen into ozone. In a bath of liquid carbonic anhydride and ether (−78°), only about 11 p.c. of the oxygen was converted. In the liquid air-bath the optimum pressure is about 100 mm., when the yield of ozone reaches about 55 grms. per kilowatt-hour. As the pressure increases or decreases the yield decreases, being about 29 grms. at 255 mm., and 37 at 45 mm. Even at −194° the spark discharge only gives about 1 p.c. of ozone, and the authors suggest that even this amount is probably due to the action of the silent discharge simultaneously occurring. The authors found that under the conditions of their experiments very little heat was produced by the silent discharge, the evaporation of the liquid air-bath being hardly appreciably greater when the electric current was passing than when it was not.

The yield of ozone produced by the action of the silent discharge varies greatly under varying conditions, which will be considered later under the section *Industrial preparation*.

Schönbein noticed the formation of small quantities of ozone when phosphorus, partially covered with water, was left in contact with air. The phosphorus is oxidised to phosphorous and phosphoric acids, traces of ozone being formed at the same time, together with some hydrogen peroxide. According to Van 't Hoff (Zeitsch. physikal. Chem. 16, 411) 4 atoms of phosphorus can cause the production of 1 mol. ozone. If the ozone remains in contact with the phosphorus it is soon decomposed again, as it oxidises more of the phosphorus. The best results are obtained by passing a rapid current of air through a tube or bottle containing moist phosphorus at about 24°, but the quantity of ozone formed even then is very small. The action does not take place at ordinary atmospheric pressure below 6°, and the optimum temperature is about 24°. Under reduced pressure the action still takes place at 0°. The addition of sulphuric acid and potassium permanganate or dichromate to the water increases the yield of ozone. Dry phosphorus does not readily cause this reaction, but it is found that if the surface of the phosphorus is kept bright by occasionally fusing it, ozone is produced without the presence of water. Pure oxygen does not readily give this reaction unless its pressure is reduced. A mixture of oxygen with three or four times its bulk of hydrogen gives rather more ozone than air does, but the reaction is dangerous, as the phosphorus may become heated to the ignition point of the mixture and cause explosion. The slow oxidation of turpentine, oil of cinnamon, and many other organic substances, is also accompanied by the formation of traces of ozone.

The action of concentrated sulphuric acid on the peroxides of barium, sodium, hydrogen, &c., and on the salts of the per-acids at low temperatures yields oxygen containing small quantities of ozone. Potassium permanganate or dichromate give with strong sulphuric acid strongly ozonised oxygen.

If pure potassium chlorate is heated pure oxygen is produced, but if the ordinary commercial salt is used or manganese peroxide or another peroxide is added the oxygen evolved contains traces of ozone.

Crystallised periodic acid when heated at 130°–135° breaks up into water, iodic anhydride, and strongly ozonised oxygen (Rammelsberg), and aqueous solutions of the acid and of the sodium salt gradually acquire the smell of ozone.

Fluorine decomposes water and this reaction, especially at low temperatures, is accompanied by the formation of appreciable quantities of ozone, amounting sometimes to 10–12 p.c. (Moissan). If water is dropped into a tube of fluorine, deep blue vapours of ozone are evolved.

Malaquin (J. Pharm. Chim. 1911, [vii.] 3, 329) has described a new and convenient method of preparing small quantities of ozone. 20 grms. of ammonium persulphate are mixed with 15 grms. of nitric acid in a flask, the air displaced by carbon dioxide and the mixture then carefully heated to 65°–75°. The reaction, which is exothermic, then proceeds spontaneously, and the resulting gas, after being freed from carbon dioxide by passing through weak potash solution, consists of 3–5 p.c. ozone, mixed with about 90–92 p.c. oxygen and 4–5 p.c. nitrogen. It is not advantageous to

use larger quantities of the ingredients than the above, nor to increase the quantity of nitric acid.

The oxygen evolved at the positive electrode during the electrolysis of strongly acidulated water contains ozone when the anode is composed of a non-oxidisable material, such as gold, platinum, lead peroxide. But under ordinary conditions the quantity formed is very small, especially if the surface of the electrode is large. The quantity of ozone produced is increased by increasing the intensity of the current, by decreasing the surface of the anode, and by reducing the temperature. Fischer and Massenez (Zeitsch. anorg. Chem. 1907, 52, 202) used as anode a narrow platinum tube coated with glass with a narrow slit cut through the glass so as to expose a very small surface of platinum. The anode was kept cool by circulating through it a current of calcium chloride solution at −14°, and the electrolyte itself (sulphuric acid with five times its volume of water, *i.e.* just below the concentration of greatest conductivity) was kept at 0°. Under these conditions they obtained oxygen containing 28 p.c. of ozone by weight. Fischer and Bendixsohn (Zeitsch. anorg. Chem. 1909, 61, 13, 153), by embedding platinum foil in glass and grinding away the edge so as to expose a line of platinum of 0·01 mm. width, have obtained oxygen containing 23 p.c. ozone. Archibald and von Wartenberg (Zeitsch. Elektrochem. 1911, 17, 812) have found that in the electrolysis of dilute sulphuric acid the yield of ozone may be considerably increased when an alternating current is passed in addition to the direct current used for electrolysis. The alternating current apparently depolarises the electrodes, in consequence of which more of the atomic oxygen liberated at the anode re-combines to form ozone than under ordinary conditions. The authors found that of the anodic oxygen produced by the direct current, as much as 37 p.c. may be evolved in the form of ozone, although, owing to the large amount of gas produced by the alternating current, the content of ozone in the total anodic gas does not exceed 12 p.c. The electrolytic preparation is convenient for laboratory work, high concentrations being obtainable, but the consumption of current is large—out of all proportion to that consumed for the silent discharge method—so that there is little likelihood of its being commercially available.

The formation of ozone being a strongly endothermic reaction, Nernst (Zeitsch. Elektrochem. 1903, 9, 891) argued, from theoretical considerations, that at high temperatures oxygen should become self-ozonised, and that at 6640° oxygen must contain 10 p.c. of its volume in the form of ozone. Much experimental work was carried out to try and produce ozone by heat alone, but without success. However, Fischer and Braehmer (Ber. 1906 39, 940), Fischer and Marx (*ibid.* 1906, 39, 3631; 1907, 40, 443), and Fischer and Wolf (*ibid.* 1911, 44, 2956), have proved the correctness of Nernst's views. The decomposition velocity of ozone at 1000° is so enormous that at that temperature 1 p.c. would be reduced to 0·001 p.c. in 0·0007 seconds. The only chance of obtaining the ozone formed at the high temperatures is, therefore, by cooling instantaneously, *i.e.* more rapidly than the decomposition velocity. This was effected by carrying on the heating or combustion in contact with liquid air or liquid oxygen. Flames of hydrogen, and acetylene of 1 c.m. length burning at the nozzle of a narrow quartz tube were plunged into and continued burning in liquid air or oxygen. Flames of CO and SH_2 could not be made to burn in the liquid oxygen, but were made to impinge on its surface. Burning sulphur and burning charcoal were thrown on to the surface of liquid oxygen. In all these cases ozone was obtained, the cooling effected by the liquid oxygen being more rapid than the rate of decomposition, the ozone formed was at once cooled and immediately dissolved in the liquid air or oxygen. When a glowing Nernst pencil at a temperature of about 2200° was plunged into liquid oxygen, ozone was produced, and when the experiment was continued for 10 hours nearly 4 p.c. of the oxygen was converted into ozone. Ozone was obtained when a current of oxygen or air was made to impinge on a glowing Nernst pencil in liquid air, or through a perforated pencil. With moist oxygen or with a fine stream of water hydrogen peroxide is also formed, and with air oxides of nitrogen are present. In the latter case, the slower the stream of air the more oxides of nitrogen are produced, the more rapid the stream the more ozone. With a stream of air of velocity above 30 metres per second ozone alone is produced, and below 5 metres per second only oxides of nitrogen. When an electrically heated platinum wire at 1700° was plunged in liquid air ozone was formed, but no nitric oxides. In liquid oxygen the platinum wire fused after disintegration, but by glazing it with zircon chloride or yttrium nitrate, the platinum wire lasted some minutes, and ozone was then produced. The arc light in liquid air produced ozone and oxides of nitrogen. In these reactions with air currents short heating and rapid cooling produced mainly ozone, long heating and slow cooling mainly oxides of nitrogen, and long heating and rapid cooling mixtures of ozone and oxides of nitrogen. In the combustion of hydrogen and of acetylene hydrogen peroxide was among the products. By varying the conditions the authors were able largely to control the formation of the various products. With the Nernst pencil in liquid air the action of the electric energy in the form of heat approximates to the same order of magnitude as it does in the silent discharge. A rapid stream of air or ozone blown diagonally against a Bunsen flame produces traces of ozone, and has been suggested as a technical method; but though the actual energy consumed in using high temperatures alone may not be excessive, the other conditions render its technical application hopeless.

The cathode rays and the ultra-violet light rays acting on air or oxygen produce ozone, and this action is much increased at low temperatures. If liquid oxygen is exposed to these rays ozone may be detected on evaporating the oxygen. If solid oxygen snow is dipped in liquid hydrogen and exposed to the ultra-violet rays, the oxygen, after evaporation of the hydrogen, is found to contain ozone (Dewar). The action of the ultra-violet rays in the sun's rays, on the upper layers of the atmosphere, is almost certainly one of the main causes of the ozone present in the atmosphere. But whilst the ultra-violet rays produce ozone from oxygen,

they also have a destructive action on ozone already formed (*cf.* Weigert, Zeitsch. physikal. Chem. 1912, 80, 78; Griffith and Shutt, Chem. Soc. Trans. 119, 1921, 1948).

The rays emanating from strongly radio-active metals and their salts produce traces of ozone when acting on air or oxygen (Curie, Compt. rend. 1899, 129, 823).

Ozone is produced in minute quantities during the evaporation of water, especially when the latter is in the form of spray, and this forms one source of the ozone present in sea air.

Properties.—In almost all its modes of production ozone is mixed with considerable and generally with very large quantities of oxygen or air. In this diluted state it has a strong and characteristic odour, somewhat resembling that of dilute chlorine, and appears colourless unless viewed through layers of several feet when its blue colour becomes visible. The odour is distinctly detected in air containing only one part of ozone in 500,000 air. Hautefeuille and Chappuis (Compt. rend. 1882, 94, 1249) first succeeded in separating approximately pure ozone by carefully compressing ozonised oxygen to 125 atmospheres pressure at the temperature of liquid ethylene (−103°).[1] The ozone condensed as a deep blue liquid, the superincumbent highly compressed gas being also of a deep blue colour. Liquid ozone mixed with some liquid oxygen is obtained when a current of ozonised oxygen is passed into a tube placed in a bath of liquid oxygen. Ladenburg (Ber. 1898, 31, 2508 and 2830), by the careful fractionation of the mixture thus formed, obtained ozone of a purity of 84·4 p.c. When strongly ozonised oxygen is bubbled slowly through liquid oxygen in a tube, a mist gradually forms above the surface of the oxygen, and after a little while a dark blue drop of liquid ozone forms just above the surface (Dewar). On raising the tube a little this drop may be brought into contact with the liquid oxygen in which it immediately dissolves. Liquid ozone is a very deep blue, almost black liquid which is transparent in thicknesses of less than 2 mm., but above that thickness is almost opaque. The boiling-point was first given by Olszewski (Monatsh. 1887, 8, 69) as −106°. A careful re-determination by Troost (Compt. rend. 1898, 126, 1751) gave −119°. The following constants are given by Riesenfeld and Schwab (Ber. 1922, 55 [B] 2088): m.p. −250°; b.p. −112°·3; critical temperature −5°; *d* −182, 1·784; density at b.p. 1·46; critical density 0·537; critical pressure 64·8 atmos. Liquid ozone is fairly stable at temperatures below its boiling-point, and may be distilled if contact with organic matter or other oxidisable impurity is avoided, but the least trace of such impurity causes violent explosion. The gaseous ozone formed by the vaporisation of the liquid is dark blue in colour and is very unstable, exploding violently on a slight rise in temperature or by contact with a trace of organic matter or easily oxidisable substance. As is natural in a strongly endothermic compound the gas gradually undergoes spontaneous decomposition. Sudden changes of pressure cause it to explode. Very varying statements have been made as to the decomposition of ozone in admixture with air and oxygen, owing, in many cases, to the presence of traces of impurities in the samples tested, but the recent researches of Chapman and Jones (Chem. Soc. Trans. 1910, 97, 2463; 1911, 99, 1811) have cleared up the doubtful points. The decomposition, which is very slow at low temperatures, is greater the more ozone is present, increases rapidly with rise of temperature—at 100° from about one-half to three-quarters is destroyed in half an hour—and is almost instantaneous at 300°. The decomposition at high temperatures is accompanied by phosphorescence, which is very marked when a hot glass rod is brought near the surface of liquid ozone (Beger, Zeitsch. Elektrochem. 1910, 16, 76; *cf.* Trautz and Seidel, Ann. Physik. 1922 [iv] 67, 527), and Dewar has noticed phosphorescence when passing ozone vapour through a capillary opening. The presence of oxygen, nitrogen, carbon dioxide, and moisture is practically without influence on the rate of decomposition, but the presence of traces of oxides of nitrogen, chlorine, phosphorus pentoxide, &c., very considerably accelerates it. Reduction of pressure also increases the rate of decomposition.

Ozone is decomposed in unlimited quantity by the peroxides of manganese, cobalt, nickel, and lead, by the oxides of copper and iron, and also by silver leaf, the oxides or silver undergoing no permanent change. These effects are probably due to the successive or simultaneous formation and decomposition of higher oxides. In the case of silver leaf the alternating formation and decomposition of silver oxide may be observed. In some cases ozone acts, like hydrogen peroxide, as a deoxidising agent on highly oxidised compounds. Thus hydrogen peroxide is reduced to water, and barium peroxide to the monoxide. In these cases the ozone is simultaneously decomposed: $O_3+H_2O_2=2O_2+H_2O$. Ozone is also decomposed when agitated with powdered glass, or by passage over spongy platinum or palladium. It is, however, without action on permanganic or perchromic acids.

Certain inorganic salts are oxidised by ozone; in some cases, as with stannous chloride, the ozone is wholly absorbed:

$$3SnCl_2+6HCl+O_3=3SnCl_4+3H_2O$$

in others, and they are the majority, only one atom of the ozone molecule reacts with the salts: $O_3=O_2+O$. Thallous salts are completely oxidised by ozone and the thallic oxide may be collected and weighed.

Sodium sulphide and polysulphide are directly oxidised by ozone to sulphite, some thiosulphate and a little hyposulphite being also formed. Sodium hydrogen sulphide evolves hydrogen sulphide, the sodium sulphide being oxidised in the manner stated. Neutral solutions of thiosulphates form chiefly sulphate and dithionate, whilst in alkaline solution oxygen is evolved and only one atom of the ozone molecule is active. A neutral solution of a sulphite reacts similarly, whilst sodium hydrogen sulphite is oxidised to sulphate and a little dithionate without liberation of oxygen (Riesenfeld and Egidius, Zeitsch. anorg. Chem. 1914, 85, 217; Chem. Soc. Abstr. 1914, ii. 262).

Very varying statements are made as to the solubility of ozone in water, some observers stating that it is insoluble. It is undoubtedly

[1] During compression care must be taken to keep the temperature from rising much, as otherwise the ozone is liable to explode with great violence.

somewhat soluble, although the degree has not yet been satisfactorily determined. Various causes are probably contributory to these discrepancies. The tests have generally been carried out with very dilute mixtures, and the experimental figures so obtained multiplied up to correspond to pure ozone. The experimental error is thus very largely increased and is further augmented by the partial decomposition of the ozone during the tests, the very great variation in solubility at varying temperatures and possible deviation from the law of solution according to partial pressures. From some of the most trustworthy results it appears to be at least ten times as soluble in water as oxygen is. Thus Carius found the coefficient at 1°=0·834, Schöne at 18°=0·366, and McLeod at 14°=0·274. Mailfert (Compt. rend. 1894, 119, 951), working with an air containing 3–5 p.c. by volume of ozone, gives the coefficient of solubility as 0·64 at 0°, 0·5 at 11·8°, 0·27 at 27°, 0·03 at 55°, and 0·0 at 60°. Ladenburg, on the other hand (Ber. 1898, 31, 2510), gives the solubility as 0·01 by volume. According to Moufang, one litre of water at 2° dissolves about 10 mg. of ozone, but only about 1·5 mg. at 28°. The solution acts as a powerful oxidiser, and has the characteristic odour of ozone. The ozone in solution gradually disappears, and simple agitation of ozonised oxygen with water destroys much of the ozone.

According to Nasini and Porlezza (Atti R. Accad. Lincei, 1912 [v.] 21, ii. 740), the acid waters of the Bagnore of Monte Amiata are ozonised in such quantity as to smell plainly of the gas, one litre of the water contains 0·135 c.c. of ozone. The gases rising from the water contain small quantities of ozone.

In presence of sulphuric acid the rate of decomposition is much smaller and experiments with 0·1 N acid at 0° give concordant values. The mean value of the absorption coefficient is 0·487, and since this, which expresses the ratios of the concentrations in the gas and solution, is independent of the absolute concentration, it follows that the molecular weight of the dissolved ozone is the same as that of the gas when this value is corrected for the salting-out action of the sulphuric acid, the absorption coefficient in water at 0° is found to be 0·494 (Rothmund).

The so-called ozone water of commerce generally contains no ozone, its activity being due to hypochlorites, nitrous acid, &c.

Carbon tetrachloride dissolves seven times as much ozone as an equal volume of water with formation of a blue colour.

Ozone is a very strong oxidising agent, giving up one-third (one atom) of its oxygen very readily. Thus it converts copper, mercury, silver, iron, and most other metals into the corresponding oxides, but this reaction appears to require the presence of traces of moisture. Only gold, platinum, and some other metals of the platinum group are unattacked. Ozone has a remarkable effect on mercury, one bubble of oxygen, containing $\frac{1}{50}$ of its bulk of ozone, being sufficient to alter the physical condition of several pounds of mercury. The mercury loses its mobility, convexity of surface and lustre, and adheres to the surface of glass. If the ozone is moist, permanent oxidation takes place, but if perfectly dry the mercury is said to recover its usual physical properties when exposed to dry air. Ozone oxidises lead sulphide to sulphate, ferrocyanides to ferricyanides, manganous to manganic compounds.

Moist ozone oxidises phosphorus, sulphur, selenium, tellurium, and arsenic to phosphoric, sulphuric, selenic, telluric, and arsenic acids respectively, ammonia to nitrous and nitric acids, and silver and lead to their peroxides. Ammonia is oxidised to ammonium nitrite and nitrate, and hydrochloric, hydrobromic, and hydriodic acids are oxidised to water and the free halogen. Traces of ozone hinder the combination of hydrogen and chlorine, and traces of chlorine hinder the formation of ozone by the action of the silent electric discharge. It liberates iodine from potassium iodide, the potassium being converted into the hydroxide: $2KI+O_3+H_2O=2KOH+O_2+I_2$. This reaction forms one of the best means of determining the amount of ozone in a gas, as the iodine liberated can readily be estimated by titration. But in large excess ozone, in presence of the alkali, oxidises some of the iodine to form iodite, iodate, and even periodate (Garzarolli-Thurnlackh, Monatsh. 1901, 22, 455; *cf.* Pring, Chem. News, 1914, 109, 73).

Ozone is without action on neutral and acid solutions of potassium iodate, but in alkaline solution oxidation to periodate takes place. Ozone is without action on the alkaline periodates.

Ozone oxidises most organic compounds, destroying caoutchouc and vulcanite, for instance, so readily that these cannot be used for making connections in its preparation. It bleaches most vegetable colouring matters (indigo, litmus, &c.), and decolorises blood.

In most of the above oxidations the volume of the gas remains unaltered, the molecule of ozone giving up one atom of oxygen to the substance and leaving a molecule of oxygen: $Cu+O_3=CuO+O_2$. Turpentine, oil of cinnamon, and many other essential oils, however, absorb the ozone molecule as a whole, and the reaction has been utilised to determine the composition of ozone. Thus, if a carefully measured quantity of dry oxygen is ozonised, the contraction carefully noted, and then the resultant gas shaken with turpentine, the ozone is absorbed with a further contraction, twice as great as the first, the remaining gas being oxygen. This points to the contraction of three volumes of oxygen to form two of ozone, and this result has been confirmed by Soret and others, who also determined the relative rates of diffusion of mixtures of ozone and oxygen and of chlorine and oxygen. The molecule of ozone, therefore, contains three atoms of oxygen, one of which is easily liberated in the nascent state, and so forms a powerful oxidiser: $O_3=O_2+O$. In certain cases of oxidation, however, the ozone molecule acts as a whole, no free oxygen being liberated. This, as originally noticed by Brodie, is particularly the case in its oxidation of gases, sulphur dioxide, for instance, being directly oxidised to sulphur trioxide $3SO_2+O_3=3SO_3$ (Riesenfeld, Zeitsch. Elektrochem. 1911, 17, 634).

Some unsaturated organic compounds containing double linkings absorb oxygen to form comparatively stable *ozonides* (*see* OZONIDES), but Molinari finds that compounds with treble linkings do not form these derivatives and proposes this reaction for distinguishing between double and treble linkings.

Hydrogen is not oxidised by ozone at ordinary temperatures, but is at 100°. Water is not directly converted into hydrogen peroxide. Carbon absorbs and decomposes ozone, but is not itself oxidised at ordinary temperatures.

Mixtures of methane and ozonised oxygen, passed through a heated tube, yield formaldehyde in amount increasing with the temperature up to 200° in presence of ammonia, forming ammonium formate (Wheeler and Blair, J. Soc. Chem. Ind. 1922, 41, 331 T.).

Ozone acts on solid or strong solutions of potash at low temperatures to form an unstable brown compound, which is probably K_2O_4 (Baeyer and Villiger, Ber. 1902, 35, 3038); this may be looked upon as a salt of an *ozonic acid* H_2O_4($O_3+H_2O=H_2O_4$). On rise of temperature, or acidifying, oxygen and traces of hydrogen peroxide are formed, but no ozone. According to Traube (Ber. 1912, 45, 2201) the freshly prepared substance has a colour resembling that of potassium dichromate, and after treatment with water or acids yields oxygen but very little hydrogen peroxide. The potassium ozonate of Baeyer and Villiger is possibly potassium heptoxide; by keeping it changes to the tetroxide, the decomposition of which by water produces hydrogen peroxide and oxygen in the molecular proportion of 1 : 1. With lime water ozone produces a granular precipitate which is probably a peroxide. With acetylene ozone reacts with explosive force.

When ozone (10–11 p.c.) is passed into liquid ammonia at −70°, an orange-red colour is produced which rapidly fades at −65° to −60°; above −60° the colour practically disappears. In the presence of a few drops of water the colour persists to −50° (Manchot, Ber. 1913, 46, 1089). Ozone also reacts with methylamine, dimethylamine, and trimethylamine. In the last case the reaction is explosive even at −60°. A 5–10 p.c. solution of trimethylamine in chloroform gives on treatment with ozone trimethylamine oxide $O:N(CH_3)_3$ which is precipitated as hydrochloride, the hydrogen chloride being formed by the action of ozone on chloroform.

If gold or platinum plates are immersed in ozonised air or oxygen they are found to have become electro-negative to other similar plates. Copper plates show similar action, but to a very much less degree.

The great chemical activity of ozone and its unstable character are largely due to the fact that it is a highly endothermic substance, and thus gives out a great deal of heat on decomposition. The following are the most important determinations by various investigators of the heat absorbed in the formation of ozone from oxygen :—

Hollman, 1868	17,064 Cals.
Berthelot, indirect, 1876 . .	29,800 ,,
Mulder and v. d. Meulen, indirect, 1882	33,700 ,,
v d Meulen, indirect, 1882 .	32,800 ,,
v. d. Meulen, direct, 1883 . .	36,500 ,,
Jahn direct, 1908 . . .	34,100 ,,
Kailan and Jahn, 1910 (Zeitsch. anorg. Chem. 68, 243) . .	34,500 ,,
Kailan and Jahn, 1910 (*ibid.*), decomp. by hot Pt wire . .	34,000 ,,

Ozone gives an absorption spectrum consisting of numerous lines, of which the two most characteristic (of wave length 609·5–595·5 and 577–560) lie close on each side of the D line. Chappuis (Compt. rend. 1882, 94, 858) mapped 11 bands lying between the wave length 628·5 and 444. Schöne (Zeitsch. anorg. Chem. 1894, 6, 333) observed 13 more or less intense lines. Ladenburg and Lehmann (Ber. Deut. physikal. Ges. 1906, 4, 125) noticed, in the spectrum of liquid ozone, a line in the red which only appears when about ¾ of the ozone is evaporated, and considered this as pointing to traces of a higher molecular modification of oxygen being present, indications of which are to be found in other characteristics of ozone. Hartley (Chem. Soc. Trans. 1881, 39, 60, and 111) found many of the dark lines of the solar spectrum to be due to absorption by ozone present in the atmosphere and considered the colour of the sky to be largely due to this ozone. Meyer (Ann. Physik. 1903, [iv.] 12, 849) confirms Hartley's result and conclusions.

Ozone is more magnetic than oxygen, the ratio of its specific magnetism to that of oxygen being greater than the ratio of their densities. For the physiological influence of ozone, *see* Hill and Flack, Proc. Roy. Soc. 1911, B. 84, 404; Jordan and Carlson, J. Amer. Med. Assoc. 1913, 61, 1007.

Oxozone. Various workers have suspected the presence in ozone of a still more condensed form of oxygen. As already mentioned Ladenburg came to this conclusion from his study of the spectrum of liquid ozone, and in conjunction with Goldstein obtained ozonides containing the group O_4. Harries (Zeitsch. Elektrochem. 1911, 17, 629), by evaporating a mixture of liquid oxygen and ozone through a series of flasks, found the sp.gr. of the gas in the first flask greater than that of the gas in the second, and that the gas in the first flask liberated more iodine from potassium iodide than corresponded to its sp.gr., whilst that in the second liberated the expected amount. He then found (Zeitsch. Elektrochem. 1912, 18, 129) that whilst, as has been generally stated, moderately ozonised oxygen may be passed through caustic potash solution and sulphuric acid without appreciable loss of ozone, this is not the case with very concentrated ozonised oxygen, at all events when the latter has been produced by the silent discharge with a high tension current. Working with a mixture containing 11–14 p.c. of ozone produced by an 8000-volt current of 10 per second periodicity, Harries found that 3–4 p.c. loss of ozone occurred when the mixture was bubbled through a solution of caustic potash and a further 2–3 p.c. if it was subsequently passed through sulphuric acid. He has further (Ber. 1912, 45, 936), in conjunction with some of his students, published the results of the action of the washed and unwashed ozone in the preparation of ozonides. He finds that butylene with the washed ozone produces the monomeric ozonide $C_4H_8O_3$ and the dimeric ozonide $(C_4H_8O_3)_2$, but that with the unwashed gas the mono- and dimeric oxozonides $C_4H_8O_4$ and $(C_4H_8O_4)_2$ are also produced (Evers). Treating tetrahydrobenzene in hexane with the washed ozone the solid ozonide $C_6H_{10}O_3$ is readily obtained, even without recrystallisation, whilst with the unwashed a mixture of the ozonide

and the oxozonide is produced (Seitz). Caoutchouc similarly yields $C_{10}H_{16}O_6$ and $C_{10}H_{16}O_8$ (Hagedor). Under the conditions in which Harries worked, he considers that of the so-called ozone about one-third was really oxozone and that the greater liberation of iodine just referred to is due to oxozone acting in a different manner from ozone on potassium iodide.

Riesenfeld and Schwab (Ber. 1922, 55 [B], 2088) find no conclusive evidence for the existence of oxozone.

Detection and determination.—Ozone is most readily detected by means of paper moistened with a mixture of starch and potassium iodide. If ozone is present, iodine is liberated, and the starch paper coloured blue. This reaction, however, is also produced by nitrous and nitric acids, by chlorine, &c., so that it is not conclusive. A more conclusive test is to take a piece of neutral litmus paper and moisten half of it with a neutral solution of potassium iodide. If now this paper is subjected to the action of ozone the potassium iodide is oxidised and caustic potash formed, which at once turns the litmus paper blue. The turning blue of the part of the litmus paper not treated with the iodide would indicate the presence of any ammonia, which might otherwise be taken for ozone. Chlorine, nitrous acid, &c., if present, would form a neutral potassium salt, or would show an acid reaction. If, then, the untreated end remains the neutral purple whilst the iodised end turns blue, the presence of ozone is fairly conclusively proved. The litmus may be advantageously replaced by phenolphthalein or rosolic acid. Papers moistened with guaiacum or with tetramethylene-*p*-phenyldiamine, both of which are turned blue by ozone, are very sensitive, but, like iodised starch paper, are also similarly acted on by other oxidising agents. Arnold and Mentzel (Ber. 1902, 35, 1324 and 2902) recommend paper soaked in solution of benzidene or of tetramethyl-di-*p*-aminophenylmethane. The benzidene is coloured brown by ozone, blue by nitrous acid, blue and then red by chlorine, and gives no reaction with hydrogen peroxide, hydrocyanic acid, sulphuretted hydrogen or ammonia. The 'tetramethyl base' gives violet with ozone, straw-yellow with nitrous fumes, deep blue with Cl or Br, and no reaction with hydrogen peroxide. The sensitiveness of the reaction is increased by adding a trace of acetic acid. Fluorescein is a very sensitive reagent for the detection of ozone. At a dilution of 1 in 1,000,000 its solution loses its fluorescence in the presence of ozone and is decolorised. At a dilution of 1 in 1000 it loses its fluorescence but the colour remains yellow. According to Benoist (Compt. rend. 1919, 168, 612), who describes an optical arrangement which permits of the detection of fluorescence in a solution diluted to 1 in 1,000,000,000, it is possible by using 3 c.c. of such a solution to detect and estimate 10^{-9} gram of ozone. For the quantitative determination of ozone the potassium iodide reaction is satisfactory. It is best to pass the ozone through the neutral potassium iodide solution and acidify before titrating. It is essential that a large excess of the iodide solution should be present, as otherwise some oxidation of the liberated iodine may occur. Baskerville and Hamor (J. Ind. Eng. Chem. 1911, 3) prefer to use cadmium potassium iodide, as the solution is more stable towards light. Ladenburg (Ber. 1903, 36, 115) obtained satisfactory results by passing the ozone slowly through standardised sodium-hydrogen-sulphite and then titrating. If the presence of oxidising agents other than ozone is suspected, two estimations should be made, the one of the gas in question, the second after the gas has been passed through a tube, heated at 260° to destroy the ozone. The difference of the two tests gives the amount of ozone present. The presence of oxides of nitrogen may also be detected by passing the mixed gases into liquid air. The ozone is dissolved whilst even traces of the oxides of nitrogen are at once solidified and may be filtered off. For the estimation of ozone in presence of hydrogen peroxide, *see* Rothmund and Burgstaller, Monatsh. 1913, 34, 693 ; also Pring. Proc. Roy. Soc. 1914, [A] 90, 204.

A rapid method of estimating small quantities of ozone in the air or in water consists in making the ozone act on a known volume of N/100 ferrous ammonium sulphate solution and titrating back with N/100 permanganate solution (David, Compt. rend. 1917, 164, 430).

The determination of the density of the ozonised air or oxygen has been used for measuring the amount of ozone present. Otto has designed a baroscopic apparatus for this purpose, and also a dilatometer for utilising for the same purpose the dilatation caused by decomposing the ozone at the temperature of boiling amyl benzoate (261°).

Ozone is present in minute quantities in the atmosphere. The maximum amount is certainly never more than 1 part in 450,000 of air. According to Pring (*l.c.*) it is 2·5 vols. per million vols., this amount varying but little between 5 and 20 kilometres high, *see also* Hayhurst and Pring, Chem. Soc. Trans. 1910, 97, 868. Its principal sources are probably the silent discharge from thunder-clouds and accompanying the flash discharge of lightning, the evaporation of water, and especially of saline waters, as in the sea foam, the action of some vegetable products on the air, and, perhaps, in the greatest degree the action of the ultra-violet solar rays on the atmosphere. Wurster found (Ber. 19, 3208) that ozone is also formed by the action of sunlight on clouds. When clouds are continually formed from above (*i.e.* in sunlight), all become laden with ozone, whilst when they are formed from below the upper layers are much more charged than the lower (*cf.* Holmes, Amer. Chem. J. 1912, 47, 497 ; Usher and Rao, Chem. Soc. Trans. 1917, 111, 799).

The ozone present in the atmosphere probably plays an important part in keeping the air pure and fresh and destroying the deleterious organic matter constantly passing into the atmosphere from decomposing flesh, animal exhalations, &c. In the open country, and especially by the seaside, ozone can always be detected, but in the air of large towns it is either absent or present in much smaller quantities. Richardson proposed (Asclepiad, 1887) the artificial production of ozone for the purpose of purifying the air of sick-rooms and even of towns, but it is only recently that this use has been practically introduced.

When present in the air in very minute quantities ozone is said to be advantageous to health,

but if the quantity present is enough to cause a strong odour it is found to have a very irritating and harmful effect on the mucous membrane and the system, producing headache, influenza, &c. If the quantity present is large it becomes a strong irritant poison, causing acute inflammation, and leading to fatal results. Slightly ozonised air and oxygen is now sometimes used medicinally, especially in pulmonary complaints. Labbé has shown that ozone to the extent of 1 part in 20,000 may be inhaled for half an hour at a time without any ill-effects.

Industrial preparation and applications.—In recent years the industrial preparation of ozone has been very greatly improved, and has developed into an important industry, which is still growing rapidly. Of all the methods of producing ozone, the only one which seems technically economical is that by the action of the silent discharge in air or oxygen. Starting from the original Siemens ozoniser innumerable modifications have been proposed, but these may be broadly divided into three classes, and only a few of the principal can be referred to here. The first class comprises those with smooth electrodes of large area either in the form of concentric cylinders or parallel plates. The second comprises those having one or both of the electrodes more or less pointed; and the third is a combination of the first and second classes, wherein the plate electrodes are so modified or roughened as to virtually transform them into a very large collection of points. The majority of the industrial ozonisers have either one or two sheets of a solid dielectric between the two electrodes, though in some the air or oxygen is alone employed as the dielectric.

As already stated, the yield of ozone varies enormously under varying conditions of character of discharge, form of electrode, quantity and potential of current, &c. These conditions, which are very complicated, have been studied by numerous investigators, especially by Warburg and Leithauser, who have published very exhaustive and important results of their experiments (Warburg, Ann. Physik, 1901, 5, 781; 1902, 9, 1286; 1904, 13, 470 and 1080; 1905, 17, 6 and 29; Ber. Deutsch. physikal. Ges. 1904, 209; Warburg and Leithäuser, Ann. Physik, 1906, 20, 734; 1909, 28, 1; Russ, Zeitsch. Elektrochem. 1906, 12, 409; Gray, Sitz-Ber. K. Akad. Wissen. Berlin, 1903, 1016; Harries, Annalen, 1906, 343, 334; Ber. 1906, 39, 3667; Askernasy, Technische Elektrochemie, 1910; H. de la Coux, L'Ozone et ses Applications industrielle, deuxième edition, Paris, 1910; de Kay Thompson, Applied Elektrochemistry, Macmillan, 1911). Reference to these researches must be made for details, only some of the general results can be summarised. If a point distant 1 cm. from a plate connected to earth is charged negatively to 7000 volts in air, a bluish light surrounds the point. On raising the potential a red brush appears separated from the blue by a dark space, the plate remaining dark. From a positively charged point a reddish light appears at a low potential and a brush develops as the potential is raised. Old points tend to lose the power of forming the brush discharge, giving a spark instead, but the brush reappears if a spark gap even of only 0·1 mm. length is introduced before the points. If an alternating current passes between a point and an earth-plate the positive brush is apparent, although by means of a revolving mirror it may be seen that the negative is actually alternately present. Between plates with solid dielectrics between them a uniform luminosity occurs with a high potential, a lower one tending to form brush discharges. As a general rule, other conditions being equal, the *yield* of ozone in proportion to the energy consumed is highest, the more the uniform luminosity can be maintained, and the lower the temperature. The highest concentration of ozone is obtained with negative points, the highest yield with positive points. For concentrations up to 4 grms. per cubic metre positive points and a high current are most economical, between 4 and 9 grms. per metre negative points and low currents (Warburg and Leithauser).

The production of ozone from oxygen by the silent discharge is accompanied by a simultaneous destruction of the already formed ozone to oxygen, the decomposition being greater the greater the quantity of ozone present and the higher the temperature. This, on the one hand, causes a limitation of the concentration obtainable, and on the other, a decreasing efficiency the higher the concentration. The technical standard of concentration is generally taken as grams of ozone per cubic metre of air or oxygen The maximum concentrations obtainable technically are about 50 grms. with air and 150 with oxygen—the concentrations and yields, under like conditions, with oxygen are about three times what they are with air—but for technical economy much lower concentrations are used. The concentrations at present employed are generally from 1 to 4 grms. per metre, the lowest concentration being selected which is consistent with the satisfactory carrying out of the process in hand. The cost per unit of actual ozone produced (*i.e.* consumption of energy per unit weight of ozone) increases rapidly with increase of concentration—an increase of concentration from 2 to 12 grms. means a loss of efficiency of at least 25 p.c. This must be borne in mind in comparing costs of ozone given in published statements, as in some cases where very low costs are claimed, the figures are based on such very low concentrations that the ozonised air or oxygen so produced is of very little technical value.

Siemens and Halske ozoniser.—This consists of an inner cylinder of aluminium and an outer one of glass. Six or eight of these are enclosed in an iron case which is filled with water, the water acting both as cooling water and as the one pole, the iron case being earthed and so charging the water. The aluminium cylinders are connected with one pole of the high-tension apparatus. The current used is 8000–10,000 volts, and about $\frac{1}{2}$ kilowatt is required for this unit.

Andreoli ozoniser.—In this, which was one of the early practical forms of ozoniser, the plates consist of serrated bands of aluminium placed side by side with the points (17,760 in each unit) of each electrode facing one another and having a glass plate between the two plates.

Otto ozoniser.—This consists of an iron cylinder through which runs an isolated rotating metallic axle on which are mounted a number of

thin aluminium discs. The cylinder is connected with the one pole, the rotating axle with the other, and the discharge passes between the cylinder and the aluminium discs. No solid dielectric or cooling is used and the voltage employed is 80,000.

Tindal-de-Frize ozoniser.—An iron half cylinder forms the one pole, and aluminium discs placed at right angles to the cylinder form the other. No solid dielectric is used and a voltage of 15,000–20,000 is employed. The whole is enclosed in a case, glass cylinders filled with glycerol being placed between the discs to prevent short circuiting or side discharges.

Abraham-Marmier ozoniser.—In this apparatus large plates a metre square are placed in pairs with a metal case filling the space between each pair. A stream of water for cooling runs through each metal case, and these cases are alternately connected to the two high-tension poles. A current of 15,000–20,000 volts is employed.

Ozonair ozoniser.—This apparatus, which is now used extensively in England and on the Continent, consists of two plates made of an aluminium alloy gauze separated by a dielectric plate of micanite. It is claimed for this apparatus that the raised parts of the meshes act as rounded points in facilitating the regular flow of the current and so avoiding sparking, and that the open character of the plates cause the air circulation to prevent undue heating and obviate the need for water cooling. Several of these pairs of plates are enclosed in a case to form a unit. The voltage used is 5000–8000.

Elworthy ozoniser.—The electrodes consist of metallic spirals surrounded by glass tubes, and the inventor claims that the spiral arrangement of the electrodes increases the yield of ozone. He employs a voltage of 11,000–12,000.

Howard Bridge ozoniser.—In this apparatus the plate electrodes are perforated with conical holes, the air or oxygen passing in through these holes. The inventor claims that in this way the air passes more completely into the zone of electrical action than when it is introduced at right angles to the direction of the current, as is usually the case.

Vosmaer ozoniser.—This consists of a series of parallel tubes each of which contains at opposite sides of the inner surfaces of the tubes two electrodes formed of strips of metal supported on porcelain insulators so that their inner edges, serrated in the form of a saw, point inwards towards each other.

Gerard ozoniser.—In this apparatus the electrodes consist of concentric metallic cylinders with dielectric cylinders of glass or mica between them. The dielectric cylinder is supported at one place only, and the electrodes are cut or split so as to allow for free expansion. The ozonisers are collected in groups of ten, and the inventor claims that very high potential currents can be used without sparking, and great economy in energy consumption thereby effected: he claims to obtain 100 grms. ozone per kilowatt-hour and to reach a concentration of 30 grms. per cubic metre (Bull. Soc. Belge de l'Electric. 1910, 449).

In the technical apparatus described the air may be drawn or forced through as is most convenient. When dry air is used and the temperature kept down, about 40–60 grms. of ozone per kilowatt-hour is obtained at a concentration of about 2 grms. per cubic metre. If oxygen is substituted for the air, about 120–180 grms. of ozone is obtained. At lower concentrations with a rapid air current somewhat higher yields are obtained, at higher concentrations with a slower current lower yields. From thermochemical considerations the theoretical yield of ozone should be about 1·2 kilos of ozone per kilowatt-hour, so that the actual yield at present is with air only about 5 p.c. and with oxygen 15 p.c. of the theoretical. It is very probable that higher efficiencies may be obtained by improved ozonisers.

Erlwein (Zeitschrift fur Sauerstoff und Stickstoff, 1911, 3, 143, 164, and 181) calculates from these figures that, including working expenses, interest on plant, depreciation and other charges, the cost of ozone, as it can now be actually technically produced from air, would be from 14*d.* to 22*d.* per kilo; from oxygen from 8*d.* to 11*d.* per kilo, to which latter figure has to be added the cost of the oxygen. This would compare very favourably with the cost of available oxygen from the oxidising agents usually employed.

At present by far the largest and most important application of ozone is in the purification of drinking-water. De Méritens in 1886 showed that if a water infected with bacteria were efficiently agitated with ozone the whole of the bacteria could be destroyed. Experiments to apply this fact to the industrial sterilisation of water were carried out in 1891 by Fröhlich and Werner Siemens, and an experimental plant was soon afterwards erected at Martinikenfeld. The first installation on a large scale was erected in 1893 by Schneller, van der Sleen and Tindal, at Oudshorn, Holland, for treating water from the Rhine, which contained from 5000 to 1,000,000 bacteria per c.c. This was followed by an experimental plant at the Hygiene Exhibition in Paris in 1895, and by an installation at St. Maur, near Paris, to sterilise two million gallons of water from the Marne per diem, both being erected by Tindal. About the same time Siemens and Halske put up large installations at Paderborn and Wiesbaden. Extended tests made by the Pasteur Institute, the Koch Institute, the Berlin Reichsgesundheitsamt, and by others conclusively proved that even on the industrial scale complete sterilisation of water can be effected by ozone. The pathogenic organisms are readily destroyed, the most resistant bacteria, as in most other antiseptic treatments, being the *bacillus subtilis*, the presence of which is harmless. Even when the water was intentionally very strongly infected with septic bacteria—in some cases to the extent of more than a million per c.c. —purification was complete. It is essential that the ozone be brought into contact with every particle of water to be purified, and for this purpose various forms of sterilising vessels have been used. The forms first used by Siemens and Halske and by Abraham-Marmier, consisted of wash towers filled with stones down which water in a fine state of division flowed, meeting an upward current of ozonised air. Otto used an 'emulsifier,' based on the principle of the Korting injector, to obtain his mixture of

ozone and water, and in the Tindal-de Frize system the ozonised air was forced into water, flowing down towers containing horizontal perforated baffle plates. In more recent plant various modifications and combinations of these methods have been employed. In the Ozonair plant an additional chamber is employed where the water is, by means of special nozzles, atomised in an atmosphere of ozonised air. The amount of actual ozone needed to insure certain sterilisation varies according to the character of the water, but averages about 2 grms. per cubic metre (220 gals.), *i.e.* in the concentration of 2 grms. per metre of air usually employed, a bulk of ozonised air equal to that of the water to be purified. It is essential that the water should be free from suspended matter, and if it is not it must be filtered previous to ozonisation. If the water contains dissolved organic matter this has a tendency to hinder sterilisation, and a larger proportion of ozonised air may be necessary. In the same way dissolved iron, which is oxidised and precipitated by the ozone, increases the quantity of the latter required.

Fresh installations have followed rapidly, and at the present time more than forty towns in Europe and America have adopted ozone purification of their water supplies. Amongst these are Petrograd (Siemens and Halske, 11,000,000 gals. per day), Nice (Otto, 10,000,000 gals.), Florence (1,000,000 gals.), Philadelphia (Vosmaer, 1,000,000 gals. of water from the Schuylkill River, which is said sometimes to contain two and a half million bacteria per c.c., a large proportion of which are septic), and Lindsay, Ontario (Howard-Bridge, 1,500,000 gals.). At St. Maur two new installations are being erected, each to have a daily output of 10,000,000 gals., one having the Siemens-de-Frise plant, the other the Otto-Abraham-Marmier. Hitherto there has been no similar plant in England, but the Ozonair Company have completed an installation to treat the water supply of Knutsford, Cheshire.

The cost of sterilisation of water by ozone must vary according to conditions, size of plant, &c. For small installations it should not exceed one penny per 1000 gals. of water, and for large installations may be less than a half-penny. The cost of each new installation at St. Maur for 10,000,000 gals. per day is to be £14,500, and from present working the engineer estimates that the cost of purification will be one-third of a penny per 1000 gals.

Portable ozone water purifying plants were used with success in the Russo-Japanese war, small plants for domestic supplies are now manufactured, and there is a small automatic plant obtainable which can be attached to the water supply tap. This consists of a modified Körting injector attached to the tap and connected with a small ozonising plant. The current is taken from the house supply, and the act of turning on or off the tap automatically starts and stops the process.

Another important application of ozone which has made great progress recently is for the purification of the air of rooms and enclosed spaces. It is now recognised that the bad effects of the close air of crowded rooms, &c., is not due to the excess of carbonic acid or of moisture present, but to the traces of various organic exhalations coming from the lungs and skins of the people and animals present. These traces of organic matter are readily oxidised by ozone, even when the latter is present in such minute proportions as to be harmless and even beneficial when breathed. It has been found that the introduction of small quantities of ozone into close air has the result of removing the 'stuffiness' and unpleasant effects, and making the air pleasant and invigorating. It has been said that it also destroys the bacteria present, but for any real bactericidal effect a concentration of at least 1 part by volume of ozone in 2000 parts of air is necessary, a proportion which could not be breathed. The fresh air from outside coming in through the ozoniser may very possibly be partially sterilised, and with the wall ozonisers where circulation of the air is caused, a part circulates through the ozoniser and may probably be partially sterilised. Large numbers of installations have been put into private houses, hospitals, theatres, and other public buildings, &c., and the process has been adopted on a large scale for the purification of the air of the Central London Tube Railway. It has also been adopted with advantage in cold-stores, slaughter-houses, and factories or workshops where unpleasant smelling work is being carried on, for deodorising generally, and in Paris in connection with the disinfection of clothing.

As ozone can now be obtained at a moderate cost, has such active oxidising properties, and in oxidising introduces no foreign matter, it should find large application in the chemical industries. It has already been largely used in the production of vanillin by the oxidation of *iso*eugenol, one company making about 200 tons of vanillin per year in this way, and largely through this the cost has fallen from about £20 to £2 per lb.

Ozone is beginning to find applications for bleaching various substances, oils, fats, waxes, sugars, fabrics, &c. It is being used in the ageing of spirits and in leather curing.

Ozone is now being largely used in breweries with good results (Vetter, Woch. Brau. 1911, 28, 13, and 26; Vetter and Moufang, *ibid.* 1911, 28, 377). Passed through yeast the latter is greatly improved and strengthened, and the introduction of ozone into the air of fermenting rooms, refrigerator rooms, &c., keeps these sweet and clean. Vetter and Moufang claim its successful use for sterilising casks, pipes, &c., but this is controverted by Will and Beyersdorf (Zeitsch. ges. Brauw. 1912, 35, 73, and 89).

Ozone is now employed for the seasoning of wood by the Otto process, which consists in submitting the wood to the combined influence of gentle heat and ozone. This effects the simultaneous evaporation of water and the oxidation of the constituents of the cell-sap.

Ozone has been recommended and used for the bleaching of flour, &c., but it is not satisfactory for this purpose, acting detrimentally on the flour itself.

As already mentioned, ozone is now being considerably employed for medical purposes.

L. T. T.

OZONIDES. The term ozonide was originally applied by Schönbein to certain metallic peroxides which, when decomposed, yield ozone. Later, Bourquelot applied it to certain organic

ozone carriers' (Chem. Zentr. 1897, ii. 45). The term is now used almost exclusively to designate the ozone derivatives obtained by t he action of ozone on various classes of unsaturat ed organic compounds.

The reaction between ozone and an unsaturated ethylenic hydrocarbon may be re presented by the equation:

$$CH_2:CH_2+O_3=CH_2(O)CH_2(O)O \quad \text{and}$$

$$(CH_3)_2C:CH\cdot[CH_2]_2C(CH_3)(CH_2)+2O_3 = [CH_3]_2C(O)CH(O)\cdot[CH_2]_2CMe(O)CH_2(O)O$$

one molecule of ozone being added on for each ethylene linking. When heated or treated with water, these ozonides may decompose in various ways:

$$\text{I.}\quad >C(O)C<+H_2O=>CO+>CO+H_2O_2$$

$$\text{II.}\quad >C(O)C<\rightarrow C(=O)O+>CO$$

$$\text{III.}\quad >C(O)C<\rightarrow >CO+>CO+O$$

II. and III. take place both in the absence and in the presence of water, whilst I. only takes place in the presence of water; carbon di- and monoxide are usually found in the gaseous products, which shows that more complex decompositions also occur. Ozonides for a long time had not been isolated because of their ready decomposition by water, and in their preparation it is necessary to exclude all traces of water, otherwise these decomposition products and not the ozonides are formed. When caustic soda is present, the alkali tends to condense and resinify the aldehydes formed in the reaction, and acids are also formed.

The ozonides of aliphatic compounds so far known are not directly precipitated on ozonisation in chloroform, methyl chloride or carbon tetrachloride, but those of the hydroaromatic and other ring system hydrocarbons, almost always separate under these conditions, often even quantitatively as thick oils or gelatinous masses; substances containing conjugated double bonds only add on 1 mol. ozone quickly, but much stronger ozone and a more prolonged reaction are necessary to complete ozonisation. If the unsaturated substance also contains a carbonyl group, a perozonide is formed, an ozone molecule attaching itself to the unsaturated linking whilst one oxygen atom of another ozone molecule becomes attached to the carbonyl group thus:

$$R\cdot CH(O)CH\cdot C(OH)(=O=O)$$

These substances have the properties of the ozonides and when treated with water or sodium bicarbonate often yield the normal ozonides

$$R\cdot CH(O)CH\cdot C(OH)(=O)$$

providing the latter are not very unstable.

Another class of perozonides is known, formed when a hydrocarbon ozonide is treated with more ozone; the oxygen atom in this case is taken up within the ozone molecule and the substances thus formed are regarded by Harries as being derivatives of oxozone O—O / O—O.

Thus the perozonide of cyclohexene

$$CH_2\cdot CH_2\cdot CH(O_4)\cdot CH_2\cdot CH_2\cdot CH$$

would be called *cyclohexeneoxozonide*, whilst the perozonide of mesityloxide

$$Me_2C(O_3)CH\cdot COH(=O)\cdot CH_3$$

would be termed *mesityloxideperozonide*. The oxozonides do not yield ozonides when treated with water; they are more stable than the perozonides and, when treated with more ozone, they may sometimes be made to combine with a fifth atom of oxygen. The constitution and structure of a large number of substances have been elucidated by the formation and subsequent decomposition of the ozonides.

Compounds containing acetylene linkings also form ozonides quickly with concentrated ozone, slowly with more dilute ozone, but these substances are very explosive and have been but little studied.

Preparation.—Oxygen containing 3–18 p.c. ozone is passed over a small quantity of the dry substance very slowly, the action being carried on for about 2 hours for every 3 grms. of ozonide formed. To moderate the reaction and to prevent explosion, the mixture and sometimes the ozone itself should be kept at a very low temperature; in the case of ethylene, however, the reaction proceeds quietly at 15°. For the same purpose, it is generally advisable to use an anhydrous solvent. The solvents formerly employed, hexane, carbon tetrachloride and chloroform, have been shown by Harries to be inconvenient as they are attacked by ozone. Benzene is dangerous, as it forms an explosive ozobenzene.

Glacial acetic acid would be a very good solvent, but most ozonides are too soluble in it and its boiling-point is too high for it to be readily distilled off or evaporated. Acetone is but slightly attacked. Ethyl and methyl chloride form very good solvents, but their cost prevents their more frequent use.

The ozonides are isolated by evaporating the solvent *in vacuo* below 20° and purified by solution in ethyl acetate and subsequent precipitation with light petroleum. Harries (Annalen, 1912, 390, 235) has shown that the abnormally large addition of oxygen frequently observed during ozonisation is due to the presence of

'oxozone' (probably O_4) in the ozonised oxygen leading to the formation of oxozonides. If the crude ozone be washed with sodium hydroxide and concentrated sulphuric acid, the oxozone is destroyed and pure ozonides are obtained.

Properties.—The ozonides are generally thick oils or colourless syrups with an unpleasant choking smell, and are mostly insoluble in light petroleum but soluble in most other organic solvents. They are generally explosive, but when they do not explode they may often be distilled *in vacuo* without decomposition; some, however, when thus treated, decompose into ozone and the original unsaturated substance. They have most of the properties of the peroxides, liberate iodine from potassium iodide and decolorise indigo and permanganate solutions. When reduced with aluminium amalgam they decompose thus:

$$Me_2C\!<\!\begin{matrix}\\ O\text{–}O\text{–}O\end{matrix}\!>\!CH[CH_2]_2\cdot CMe \;\begin{matrix}\\ \|\\ O{=}O\end{matrix} \;+4H$$
$$=Me_2CO+OCH[CH_2]_2COMe+2H_2O$$

or if the reaction is carried further, then with

$$10H=Me_2CH\cdot OH+OH[CH_2]_2CH(OH)Me+2H_2O$$

The ozonides of the higher aliphatic unsaturated hydrocarbons, containing one double bond and also those of the hydroaromatic hydrocarbons with one or two double bonds are, comparatively, very stable, but those of aliphatic hydrocarbons containing two double bonds are very readily decomposed. The 6- and 7-ring compounds seem to have similar stabilities towards boiling water, but the 5-ring compounds are much less stable than the two former classes. The ozonides of substances containing oxygen are very readily decomposed.

A large number of ozonides have been prepared, of which the following may be described:

Ethylene ozonide $CH_2\cdot CH_2$ with O_3 bridge is obtained by treating an absolutely dry solution of ethylene in methyl chloride with dry 7 p.c. ozone at about −70°, until the solution commences to be coloured blue. It forms a transparent colourless oil, b.p. 18°/16 mm., with a pungent odour, is readily volatile and explosive. If the ozone used is of higher concentration or the reaction is continued beyond the production of the blue colour, an *oxozonide* $C_2H_4O_4$ is formed (Harries and Koetschau, Ber. 1909, 42, 3305).

The ozonides and oxozonides of the homologues of ethylene are generally explosive, unstable substances, and have been obtained similarly, using ethyl chloride as solvent.

Ethyl alcohol, when treated with a stream of concentrated ozone, yields a peroxide, which has some of the properties but is not identical with ethyl hydroperoxide $C_2H_5O\cdot OH$.

Aliphatic aldehydes, when treated with ozone, yield peroxides of the type RHC : O : O, which have not been obtained pure, owing to the readiness with which they are transformed into the isomeric acid.

Diallyl diozonide $CH_2\cdot CH\cdot[CH_2]_2\cdot CH\cdot CH_2$ with O_3 bridges is formed by passing ozone into a chloroform solution of diallyl, is a colourless syrup which, when heated, yields succinic dialdehyde and a little succinic acid.

Allylalcohol ozonide $CH_2\cdot CH\cdot CH_2OH$ with O_3 bridge is a transparent syrup which decomposes at ordinary temperature.

Allylacetone perozonide $CH_2\cdot CH\cdot CH_2\cdot CCH_3$ with O_3 bridge, $\|\ O{=}O$ is a clear explosive syrup which decomposes on treatment with water forming formaldehyde, lævulic aldehyde and hydrogen peroxide.

***iso*Crotonic acid perozonide**

$$CH_3\cdot CH\cdot CH\cdot C\!<\!\begin{matrix}OH\\ O{=}O\end{matrix}$$
(with O_3 bridge)

is a yellowish clear explosive syrup, which on standing, evolves oxygen and yields *iso*crotonic acid, whilst with water it yields acetaldehyde, glyoxylic acid and hydrogen peroxide.

Mesityloxideozonide $Me_2C\cdot CH\cdot CO\cdot CH_3$ with O_3 bridge is obtained by treating 10 grms. well-cooled freshly distilled mesityl oxide with 12–14 p.c. ozone and a current of well-cooled carbon dioxide for about five hours, when a sample no longer decolorises an acetic acid solution of bromine. It is a thinner and less explosive oil than the perozonide, is miscible with all solvents except light petroleum and is readily decomposed by water and on heating.

When the mesityl oxide is saturated with ozone, *mesityloxideperozonide*

$$Me_2C\cdot CH\cdot C(O\cdot O_3)\cdot O\cdot CH_3 \quad (=O)$$

is formed as a thick green oil, highly explosive and spontaneously inflammable.

Methylheptenone yields similar normal and perozonides.

Phorone yields a monozonide and a diozonide —the latter being formed only very slowly when the treatment with strong ozone is very prolonged.

Oleic Acid Ozonides.

The *normal monozonide* $C_{18}H_{34}O_5$ is formed when oleic acid in acetic acid solution is treated with 0·5–18 p.c. ozone until a sample no longer decolorises a bromine solution of glacial acetic acid; or by washing the perozonide with water and sodium bicarbonate. It is a colourless, transparent, viscous liquid, heavier than water and when warmed with aqueous caustic soda yields a pleasant sharp-smelling product, b.p. 90°. When treated with water it yields nonaldehyde, pelargonic acid, azelaic acid and an aldehyde product which, on oxidation, yields azelaic acid. The reaction is explained thus:

I. $CH_3(CH_2)_7CH(O\text{–}O\text{–}O)CH[CH_2]_7CO_2H$

$$=CH_3[CH_2]_7COH+\begin{matrix}O\\ |\\ O\end{matrix}\!>\!CH[CH_2]_7CO_2H$$

II. $CH_3[CH_2]_7CH(O\text{–}O\text{–}O)CH[CH_2]_7CO_2H$

$$=CH_3[CH_2]_7CH\!<\!\begin{matrix}O\\ |\\ O\end{matrix}+COH[CH_2]_7CO_2H$$

thus the primary products are nonaldehyde, nonaldehyde peroxide, azelaic acid half aldehyde (which is a decomposition product of almost all the ozonides of the higher aliphatic unsaturated acids), and the peroxide of the latter. By the isomerisation of the peroxides, pelargonic and azelaic acids are then formed. When warmed with glacial acetic acid the same products are obtained, but more peroxides are formed, whilst if formic acid is added to the acetic acid, considerably more aldehydes result. Similar products are also obtained by reducing the ozonide with sulphur dioxide or with aluminium amalgam in aqueous solution. Unstable ammonium, copper and sodium salts of oleic ozonide have been obtained.

Oleic acid perozonide

$$CH_3[CH_2]_7CH\cdot CH[CH_2]_7COH \quad (\backslash O_3 /,\ O{=}O)$$

is formed when a glacial acetic acid or carbon tetrachloride solution of oleic acid is treated with 10–12 p.c. ozone for an hour for each gram of acid. It is a somewhat thicker liquid than the ozonide but has similar chemical properties to the normal ozonide. When oleic acid is treated with 10 p.c. ozone for a very long time (3 hours per gram) or for a somewhat shorter time (4 hours for 5 grms.) with 16–18 p.c. ozone, it yields a *superperozonide* $C_{18}H_{34}O_7$, possibly $CH_3[CH_2]_7CH\cdot CH\cdot[CH_2]_7\cdot CO_3H$ ($\backslash O_4 /$), which is a colourless substance, not much more explosive than the other ozonides and has the same general chemical properties.

Elaidic acid yields a normal and a perozonide which seems to differ little if at all from those of oleic acid.

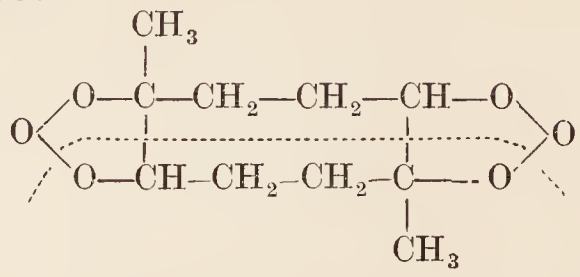
Citronellic acid yields a similar ozonide, per- and superperozonide (Harries and Himmelmann, Ber. 1908, 41, 2187).

Cholesterol ozonide $C_{27}H_{46}O_5$, which is probably an oxozone derivative, forms a very stable white powder and, when boiled with water, yields hydrogen peroxide, aldehydes and much resinous products. Similar ozonides of cholesterol derivatives have also been obtained (Diels, Ber. 1908, 41, 2596; Langheld, *ibid.* 1023).

The most interesting application of the formation of ozonides to the elucidation of the structure of a compound is perhaps that of rubber. When the latter is treated with 5·5–6 p.c. of ozone, in chloroform solution for one hour for every gram, and the product evaporated *in vacuo* below 20° and the residue purified in the usual way, a *diozonide* $C_{10}H_{16}O_6$ is formed as a yellow thick oil. It dissolves in various solvents yielding, not colloidal, but ordinary solutions, and when boiled with water or distilled with steam it yields lævulic aldehyde and acid, and lævulic aldehyde superoxide. The formation of this ozonide and its decomposition products, together with the fact that when heated, rubber yields, amongst other products, *iso*prene and dipentene, has led Harries to give the following formula to rubber:

$$\left[\begin{matrix} CH_3C{-}CH_2{-}CH_2 \\ CH \end{matrix} \gtrless \begin{matrix} \rangle CH \\ CH_2{-}CH_2{-}C\cdot CH_3 \end{matrix}\right]_x$$

which agrees very well with its other known reactions. With ozone, it would form the diozonide:

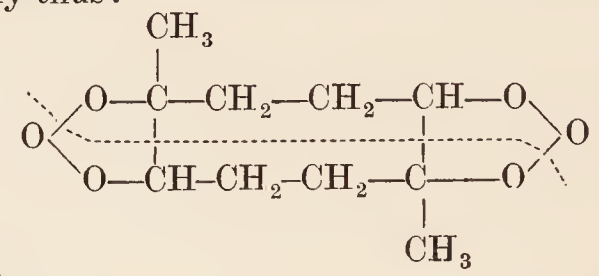


which, on decomposing, breaks at the dotted lines and therefore yields:

$$O:O:C(CH_3)\cdot CH_2\cdot CH_2\cdot CH:O:O$$
$$+ OCH\cdot CH_2\cdot CH_2COCH_3$$

Lævulic aldehyde diperoxide is readily transformed to the aldehyde in the presence of steam, consequently the lævulic aldehyde is present in large quantity (Harries, Ber. 1905, 38, 1195).

Gutta-percha gives a diozonide which seems identical with rubber diozonide, but on decomposition with water it yields much less aldehyde and more acid: its decomposition has therefore been represented as taking place chiefly thus:

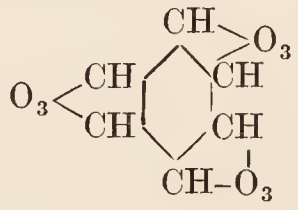


yielding:

$$OC(CH_3)\cdot CH_2\cdot CH_2\cdot CH:O:O + O:OCH\cdot CH_2\cdot CH_2\cdot C\lessgtr \begin{matrix} O \\ CH \end{matrix}$$

the latter readily being transformed into acid. The difference in behaviour of the two ozonides on decomposition is assumed to be due to some form of stereo-isomerism (*ibid.* 3985).

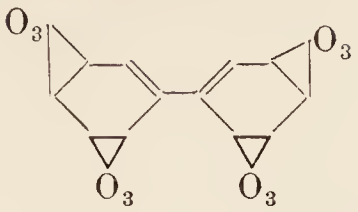
Benzene triozonide or **ozobenzene**



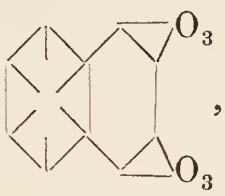
is formed by passing absolutely dry 5 p.c. ozone into dry benzene at 5°–10° for about 2 hours. It is stable in dry air at the ordinary temperature and forms a white amorphous mass which, if quite pure, becomes crystalline when treated with water at 0°. It is soluble in acetic acid but not in other organic solvents. When warmed quickly it explodes violently, and when treated with water it yields chiefly glyoxal OHC·CHO and some glyoxylic acid which probably results from the oxidation of the aldehyde with the hydrogen peroxide formed in the first reaction. These reactions show almost conclusively that benzene has three double linkings and that Kekulé's structural formula for benzene is correct.

Only the decomposition products of the triozonides of toluene *o*- and *m*-xylene and of mesitylene have been obtained.

Diphenyl forms a *tetraozonide*



obtained as a crystalline mass, which explodes violently when heated. The fact that two more ozone molecules are not added at the double linkings is probably due to steric hindrance.

Naphthalene, when strongly cooled and submitted to the action of ozone, yields a crystalline *diozonide*, thus  , indicating that, in all probability, only one of the rings has the benzene or Kekulé structure, whilst the other, possibly, has the concentric form. When treated with water the diozonide yields phthalic aldehyde $C_6H_4(CHO)_2$, phthalic acid, glyoxal, and glyoxylic acid.

Phenanthrene when treated similarly also forms a diozonide $C_{14}H_{10}O_6$ having similar properties to the naphthalene diozonide.

Tetrahydrobenzeneozonide $C_6H_{10}O_3$, obtained by passing ozone into a chloroform solution of the unsaturated hydrocarbon, forms elastic lumps, sparingly soluble in most solvents, and when boiled with water yields *n*-adipic acid and a little of the corresponding aldehyde.

m-**Dihydroxylene** yields a diozonide

$$C_6H_6Me_2O_6$$

which, on purification, forms a clear syrup with a characteristic smell. It is comparatively stable, but sometimes explodes with great violence (Harries and Neresheimer, Ber. 1906, 39, 2846).

Ozone has been suggested as a reagent for the study of the phenomena of tautomerism (J. Scheiber and P. Herold, Ber. 1913, 46, 1105; Annalen, 1914, 405, 295). It does not act catalytically in effecting the ketoneol change, and its reaction is confined to the enolic forms. The advantages of the process are that it can be carried out at low temperature and apparently without effecting structural alterations. For example, the ozonide of benzoylacetone on decomposition gave an almost theoretical yield of benzoic acid, together with methyl glyoxal, showing that under the conditions present the benzoyl acetone is enolised to $C_6H_5C(OH) : CH{\cdot}CO{\cdot}CH_3$.

Literature.—Harries, Annalen, 1905, 343, 311; *ibid.* 1910, 374, 288; Ber. 1912, 45, 809; Lebédeff, J. Russ. Phys. Chem. Soc. 1910, 42, 949; Drugman, Chem. Soc. Trans. 1906, 939; Dyckerhoff, Autoxydation organischer Stoffe, Inaug. Dissert. Karlsruhe, 1910; Valeur, Action de l'Ozone sur les composé Organique, Paris, 1909; Molinari, Ber. 1906, 39, 2735; 1907, 40, 4154.

P

PACHNOLITE (*πάχνη*, rime). A fluoride of aluminium, calcium, and sodium, occurring as an incrustation or efflorescence on cryolite. It is regarded by Knop as a hydrated cryolite in which two-thirds of the sodium are replaced by calcium (A. Knop, Annalen, 127, 61).

Composition.—

Al.	Ca.	Na.	F.	H_2O.
13·43	17·84	10·75	49·78	8·20=100·00

PACKFONG or **PACKTONG.** A Chinese alloy resembling nickel silver, and of a similar composition *v.* NICKEL.

PACO or **PACOS.** A Peruvian term for a ferruginous earth or ore containing small quantities of metallic silver.

PÆONIN (*Red Corallin* or *Aurin R.*) *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PAINT OILS. Under this term are comprised those vegetable oils which are used as vehicles for applying pigments to the surface of bodies, either as a preservative or for decorative purposes. Only the vegetable drying oils are useful; the paint oil, *par excellence*, is linseed oil. The semi-drying oils, such as cottonseed oil and maize oil, are unsuitable as paint oils. Nor is soya bean oil suitable as a paint oil, although when the price of linseed oil was high it was largely used as a substitute for linseed oil or to adulterate linseed oil. Fish oils, which are used as adulterants to an enormous extent, are unsuitable as paint oils, notwithstanding frequently made statements to the contrary. Adulteration with rosin oil is practised on an extensive scale, although more easily recognised than adulteration with animal and vegetable oils of somewhat lower iodine value than linseed oil. Oil extracted by solvents is not suitable as a paint oil. J. L.

PAINTS. *Definition.* — Coloured mixtures, usually liquids, with which suitable surfaces can be coated by a brush or other means. The coverings formed may be dull or lustrous, and often act as protectives and preservatives of the surfaces beneath. Usually, paints differ from varnishes in yielding coatings possessing less lustre in the absence of resinous ingredients, but enamel paints and various special products are of exceptional composition. Ordinary paints consist essentially of three parts, the *pigment*, the *medium* or vehicle, and the *drier* or siccative. Paints manufactured for particular uses, such as luminous paints, anti-corrosive paints, and waterproof paints, contain other components of the most diverse kinds.

Surfaces only are covered by paints: dyes stain throughout. This distinction is maintained in the present article, from which is excluded the consideration of dyes. The term ‘ pigment ’ will be confined to those substances to which paints owe their colours; mostly dry powders, finely diffusible but insoluble in the binding and thinning media employed. ‘ Paint ’ will be employed in reference to the combination of pigment and medium, ready for use by the painter. Pigments will first be described,

and then the vehicles by which these pigments are converted into paints. Driers come next in order: lastly, paints themselves.

Pigments. *Definition.*—Finely divided insoluble coloured powders, yielding paints when intimately mixed with suitable media.

Origin.—Pigments are obtained from mineral, vegetable, and animal sources, chiefly the first-named. Inorganic pigments comprise minerals and manufactured products, mostly metallic salts or oxides: such pigments are usually more permanent than those of vegetable or animal origin.

Characters.—1. Hiding power, *i.e.* the property of completely covering and concealing the surface beneath, which is measured by the greatest area over which unit mass, mixed with a given medium to painting consistency, can be uniformly spread so as to obliterate completely a coloured design. 2. Covering or spreading power, which is measured by the greatest area over which unit mass of a substance, mixed to a painting consistency with a given medium, can be uniformly spread with a brush. 3. Staining or colouring power, *i.e.* the relative degree to which unit weight of pigment will confer colour on another pigment to obtain the same degree of tone value. 4. Oil absorption power, *i.e.* the minimum quantity of oil required to convert unit weight of dry pigment from a powder to a definite paste (H. A. Gardner and R. E. Coleman, Circ. 85, Ed. Bureau, P. M. Ass., U.S.A.). 5. Durability or permanency, *i.e.* ability to stand light and weathering agencies for prolonged periods. 6. Colour or hue: the hue of a pigment is defined as the optical effect produced by it on our colour sense.

The opacity is proportional to the mass of pigment per unit volume of the paint, whereas the hiding power is independent of the amount of oil used.

Pigments may be of all degrees of opacity, and they also differ greatly in density and in the state of aggregation of their particles. Some are opaque and amorphous, others are crystalline and translucent or transparent. The opacity of a pigment depends to a large extent on its power of reflecting light, and when the ratio of refractive index of the pigment to that of the medium is less than 1 : 1 the pigment becomes transparent and is almost without obliterative effect, or in other words has no body, as in the case of terra alba or transparent pigments, *e.g.* crimson lake and Prussian blue. Such pigments are only useful for their colouring power and are known as stainers. The refractive effect of a pigment is a function of the size of the particles. The greater the covering power the less is the opacity and *vice versa*. The covering powers of white lead, barytes, zinc oxide, gypsum, and lithopone are 760, 1144, 1152, 1440, and 1500 respectively. For comparison of the hiding power of pigments, *see* J. Pfund (J. Franklin Inst., 1919, 188, 675). The colouring or staining power is dependent upon the proportion of light absorbed by a substance compared with the total amount of incident light. Samples of Prussian blue are compared for staining power by determining the relative amounts of white pigment necessary to obtain pale blues of similar 'tone' or light reflecting value. The relative staining power can be tested by a tintometer (Lovibond's). Colouring power is generally tested by comparison with a standard sample by ascertaining how much of another pigment each will colour to a given depth. The two properties of opacity and staining power do not necessarily bear any relationship towards each other, *e.g.* Prussian blue is a pigment of high staining power and very low opacity, Indian red possesses great staining power and high opacity, whilst the chromes possess moderate staining power and high opacity. The high opacity of most black pigments is probably accounted for by their power of absorbing light to a great degree as well as by their high state of subdivision. The degree of fineness is an important characteristic of pigments, and varies with the time of grinding and with the type of the mill used (Klein and Hulme, J. Oil and Col. Chem. Ass., 1920, 3, 177). A reliable method of testing the fineness of pigments is by means of an elutriator (Schöne, Zeitsch. anal. Chem., 1868, 7, 29; Lowry, J. Oil and Col. Chem. Ass., 1922, 5, 92). The use of screens of fine mesh is not satisfactory. The diameters of pigment particles may be measured microscopically, and a pigment may be regarded as finely ground for general purposes of paint manufacture when the diameters of 99 p.c. of the particles do not exceed 10μ. The hiding power is increased by finer subdivision. Crystalline powders, however impalpable, have less opacity than amorphous powders, hence the superiority of the latter as regards covering power. The oil absorption power has a marked influence on the behaviour of a paint film on exposure and varies with the nature of the pigment. The oil absorption powers of white lead, zinc oxide, red oxide, vandyke brown, barytes, and Paris white, are 7·5, 22, 10, 40, 7, and 18 respectively.

The bulk or gallonage of paint that may be produced from any pigment is inversely proportional to the specific gravity of the pigment. With specific gravity figures available it is possible for a paint grinder to calculate the yield of any specified formula. The fraction of a gallon bulked by 1 lb. of pigment is the bulking value. It must be remembered that a slight shrinkage occurs in grinding, due to elimination of air and the wetting of pigment by the oil.

The drying quality of a pigment (in an oil paint) depends upon its power of oxidising or promoting the oxidation of the medium with which it is mixed: this property is possessed in a much greater degree by some pigments than by others, and siccatives must be added when the pigment is known to be deficient in this characteristic. Permanency is tested by the power of the pigment, when made into paint, of resisting the action of light, moisture, fœtid gases, acid and alkaline vapours, exposure to the atmosphere, &c. In special circumstances, for the colouring of a lime-plastered surface, for fresco work or the like, pigments must be unaffected by lime. As a rule pigments are more durable when used in aqueous media. Instances are known of pigments in admixture exercising a detrimental influence upon one another, but in oil media this action is rarer than has been supposed. Colour or hue depends not only on the absorptive power for light, but upon chemical composition, molecular constitution and mode of production. The exact

shade is a resultant of many niceties of detail during the processes in the colour factory. Where a pigment has been precipitated from the solution the shade may vary with the amount of care devoted to the washing of the precipitate—a very small percentage of impurity being the cause of a marked difference in quality. The degree of subdivision of a pigment has a most important influence on the shade.

Colour matching.—The measurement and registration of colours in numerical terms has been attempted by many investigators. One of the best known instruments is that of J. W. Lovibond, known as the 'Tintometer.' In order to determine the hue accurately it is necessary to examine the pigment by means of a spectroscope. An absolute method of assaying pigments for hue may be founded on the use of an instrument devised by Abney and named by him a 'colour patch' apparatus. Other methods of colour measurement have been suggested (Lawrence, Proc. Oil and Col. Chem. Ass., 1919, 2, No. 6; Bawtree, Proc. Oil and Col. Chem. Ass., 1919, 2, 61). Mees (J. Ind. Eng. Chem., 1921, 729) states that the easiest method

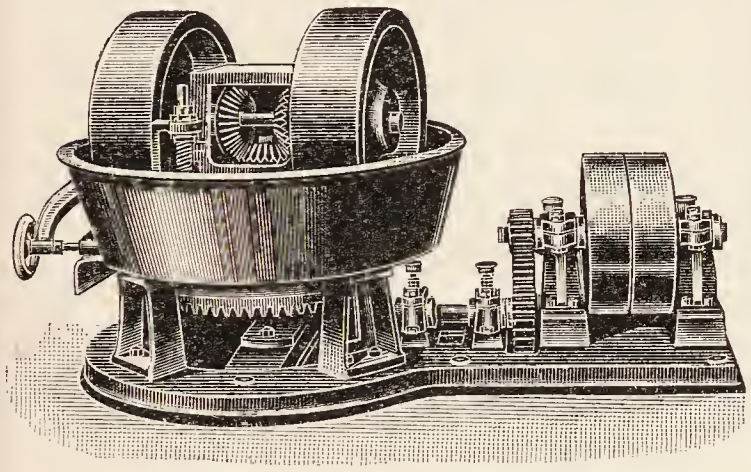


FIG. 1.

Positive-driven Edge Runner Mill (Brinjes and Goodwin, Ltd.).

of specifying hue is by means of the wave length in the spectrum, which corresponds to the hue in question. He has devised a colorimeter which expresses the colour in absolute units. The precipitated pigments are usually finer and brighter in shade in direct proportion to the dilution of the solutions employed.

Fineness of grinding involves consistency or flow. Bingham and Green (Am. Soc. Test. Mat., 1919, 19, 640) have shown that paint is a plastic body and its consistency depends on its mobility and on its yield value as determined by their plastometer. Its consistency depends also on the degree of wetting of the pigment by the medium and on the sizes of the pigment particles. As the particles become finer the tendency to flocculation increases, and unless counteracted by the dispersive power of the vehicle changes in consistency and applicability of the paint may ensue: this is of importance in the selection not only of the medium but of the pigment (F. P. Ingalls, Circ. 135, P. M. Ass., U.S.A.).

Preparation.—The pigments of commerce are so numerous that it will be impossible to describe the manufacturing processes by which most of them are obtained; but the important operation of grinding must be mentioned. All pigments must be in an extremely fine state of division. The colours used by house-painters and paper-stainers are pulverised and mixed by paint-grinders, while the more numerous and brilliant pigments used in the fine arts are ground by artists' colourmen. Formerly, most pigments were ground by hand on a grinding

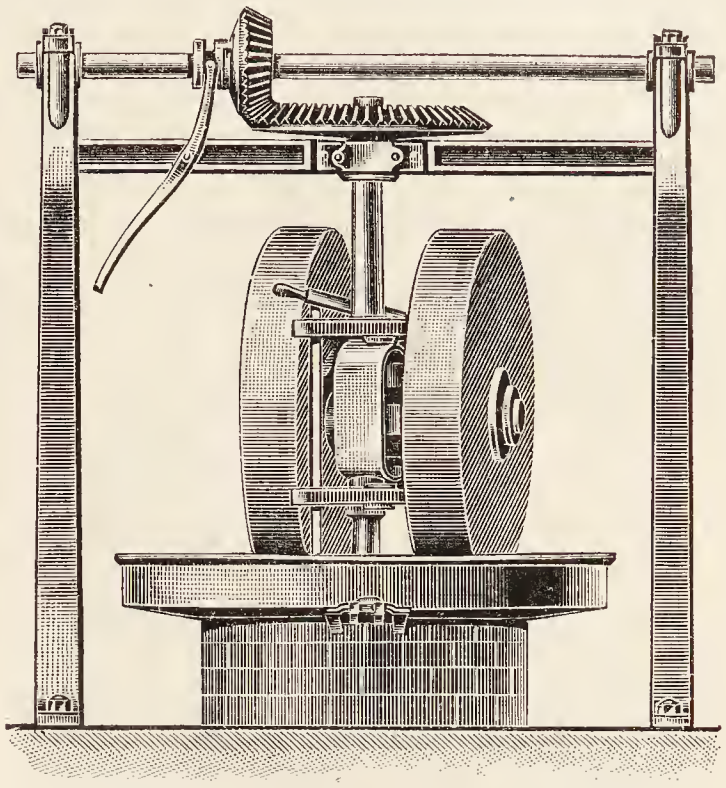


FIG. 2.

Edge Runner Mill, over-driven (Brinjes and Goodwin, Ltd.).

stone with the aid of a muller, but the unhealthy and dangerous nature of the operation, especially when orpiment, white and red leads, chrome yellow, and many other important pigments, were treated, led to the introduction of colour mills, in which larger quantities of pigments can be ground and mixed in covered

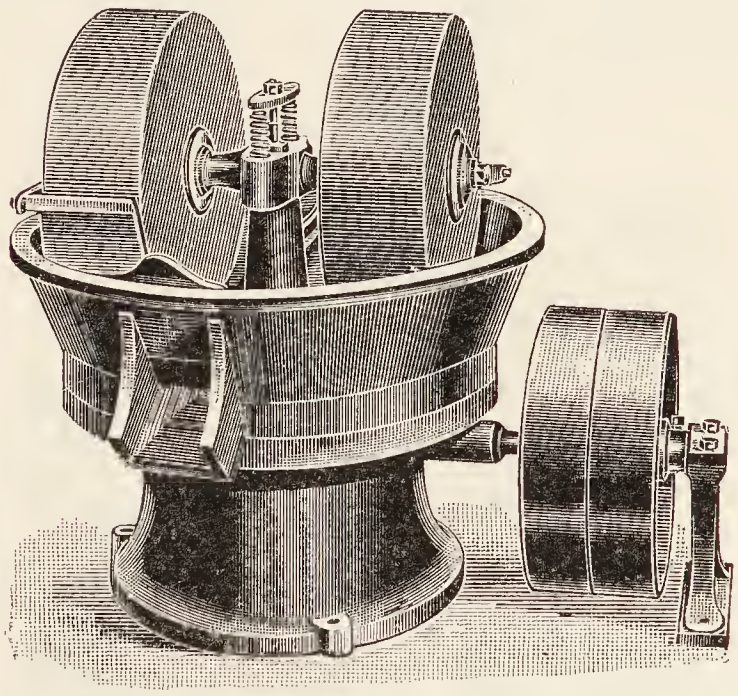


FIG. 3.

Under-driven Edge Runner Mill (Wm. Gardner & Sons, Ltd., Gloucester).

vessels, so that the risk to the workmen is very greatly lessened.

In the preparation of natural pigments levigation plays an important part to effect the separation of gritty matter and other impurities. The principle of the process depends on the fact when fine particles of a comparatively

light material, mixed with coarser particles of the same material or with particles of a heavier material, are agitated with water and then allowed to stand, the coarser and heavier particles will

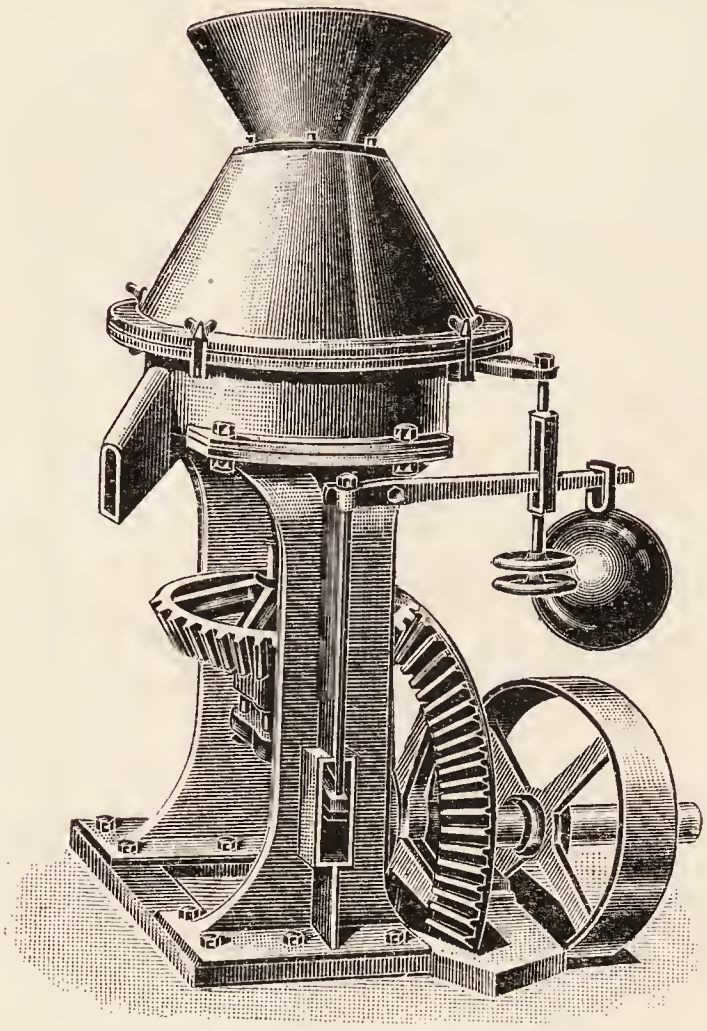


FIG. 4.

Conoidal Mill (Bryan Corcoran, Ltd.).

fall first, while the lighter particles will form a layer on the top of the coarse particles. In many cases levigation is a subsequent operation to grinding, and sometimes the two operations are combined in one plant. The separation of the fine from coarse particles may be brought

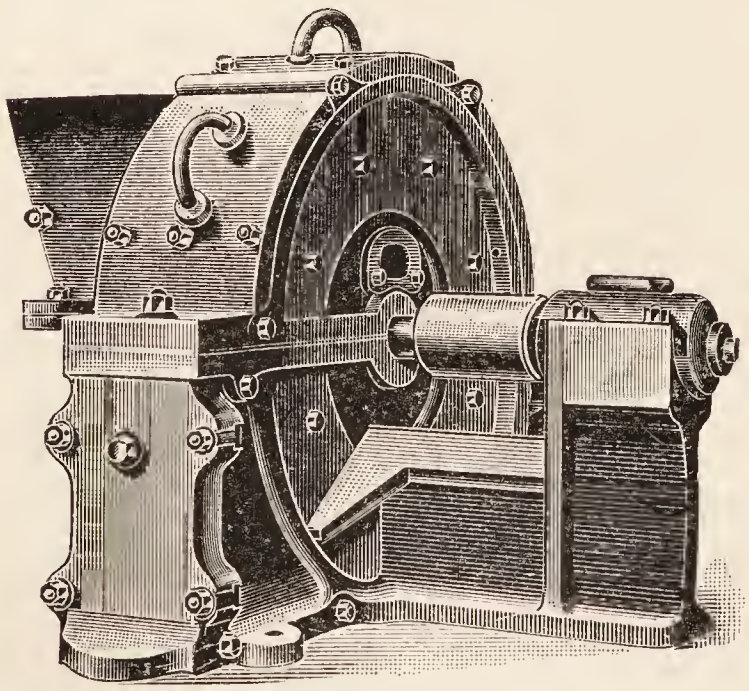


FIG. 5.

A Disintegrator (Wm. Gardner & Sons, Ltd.).

about by centrifuging the sludge (W. J. Gee, J. Roy. Soc. Arts, 1912). Many pigments are prepared by a process of precipitation.

Colour grinding.—On the larger working scale, pigments are *dry-ground* chiefly in under-driven edge-runner mills: on a somewhat smaller scale, cone mills, which are especially serviceable for materials composed of soft fragments, may be used. The centrifugal mills known as 'disintegrators' are exceedingly convenient. Fig. 1 shows one of the positive-driven edge-runner mills, maufactured by Brinjes and Goodwin, Ltd., of Whitechapel. In this type

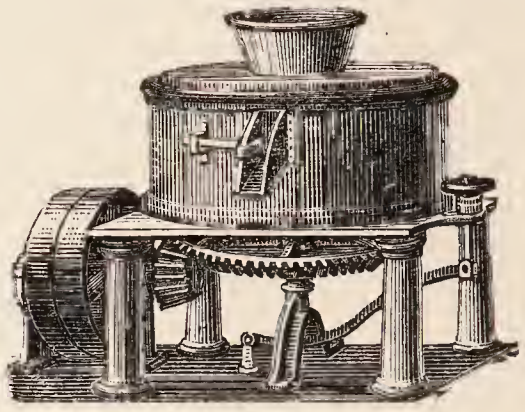


FIG. 6.

Flat Stone Mill (Brinjes and Goodwin, Ltd.).

of machine the rotation of the runner is not due to friction between its face and the surface of the pan, but is geared directly or positively with the driving shaft. Another type of edge-runner mill, top-driven, is represented in Fig. 2. The third illustration shows an under-driven mill of a similar description (Wm. Gardner & Sons, Ltd., Gloucester). The bottom-driven type of mill is for colour-grinding preferable to, and now more generally used than, the top-driven kind. The bed and runners of these mills for colour-making should be granite or porphyry. When large fragments of highly resisting materials have to be dealt with a less rigid form of mill than the positive-geared is to be recommended.

A cone-grinding mill, supplied by Bryan Corcoran, Ltd., London, is shown in Fig. 4, and in Fig. 5 is represented a disintegrator (Wm. Gardner and Sons, Ltd., Gloucester). High-speed cone-grinding mills are a great advance in obtaining fineness and rapidity of output.

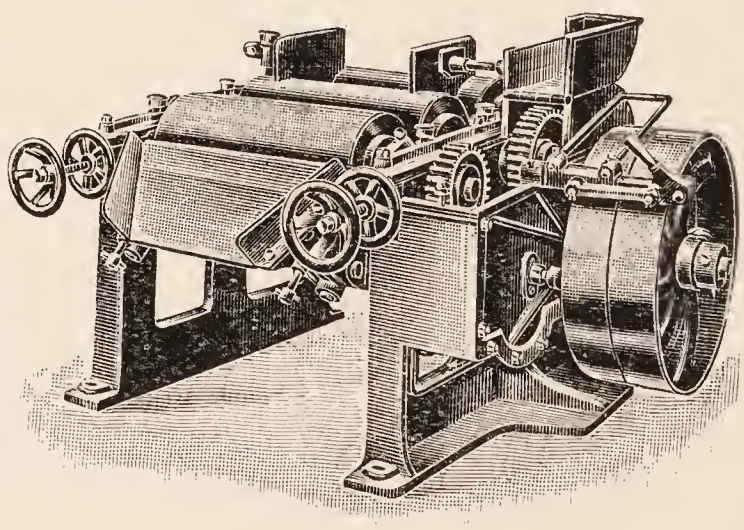


FIG. 7.

Torrance's "Quadrant" Triple Roller Mill (showing gear box open for inspection).

Pigments may be *wet-ground* in a levigating edge-runner; in a pulveriser of special construction, such as the 'Alsing' pulveriser (ball-mill, depending on the crushing action of steel balls in a revolving drum), or, if the required output be small, in a levigating flat-stone mill. Edge-runner mills are mostly used.

Paint grinding.—The older type of machine

for the *grinding of mixed paints* was the ordinary flat-stone mill (Fig. 6), but the triple-roller grinding mill (Figs. 7 and 8) has almost entirely superseded it.

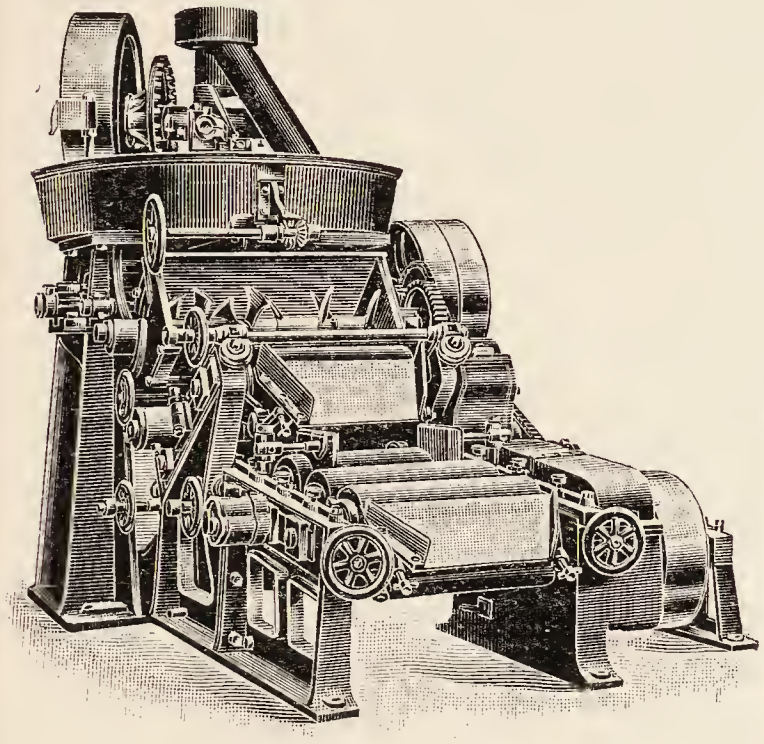


FIG. 8.

7-ft. "Torrance" Combination Silent Quadrant Triple Roller Mills.

In the Torrance patent silent roller mill, Fig. 7, there is a combination of three granite rollers geared at differential and increasing speed from

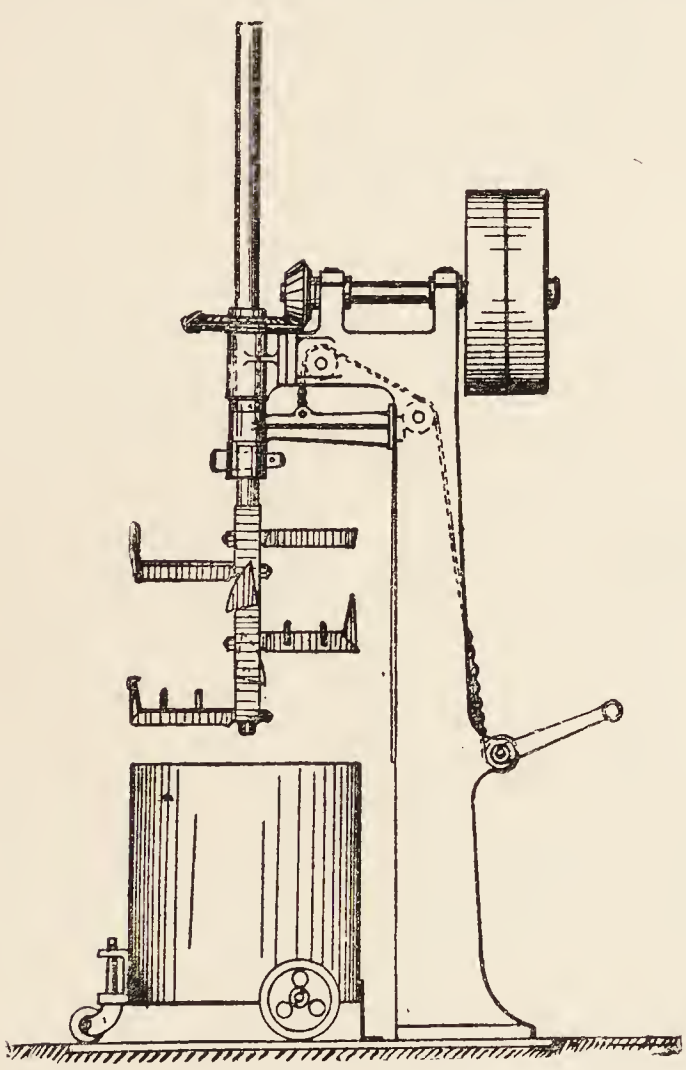


FIG. 9.

Ready-mixed Paint Mixer, with Double-acting Stirrers (Brinjes and Goodwin, Ltd.).

back to front (feed to delivery) through quadrants, *i.e.* intermediate spur-wheels enclosed in oil baths. A lateral motion is imparted to the middle roller by a differential gear, ensuring even wear of the rolls and avoidance of ridges. Fig. 8 shows the Torrance combination mill, embodying the pan mill automatically delivering to a pair of roller mills in tandem. For the satisfactory grinding to a stiff paste of pigments in two mutually immiscible media, *i.e.* oil and water as in patent driers, the flat-stone mill consists of two granite discs superposed in a horizontal plane with the lower disc fixed, and the contact faces of the stones are grooved.

Paint mixing, which precedes the grinding, is usually conducted either in a vertical mixer similar to that shown in Fig. 9, or in a horizontal mixer, which may be of the kind depicted in Fig. 10. In certain cases, however, as in the mixing of zinc paint, a positive-geared edge-runner mill, Fig. 1, is the best to use. If a

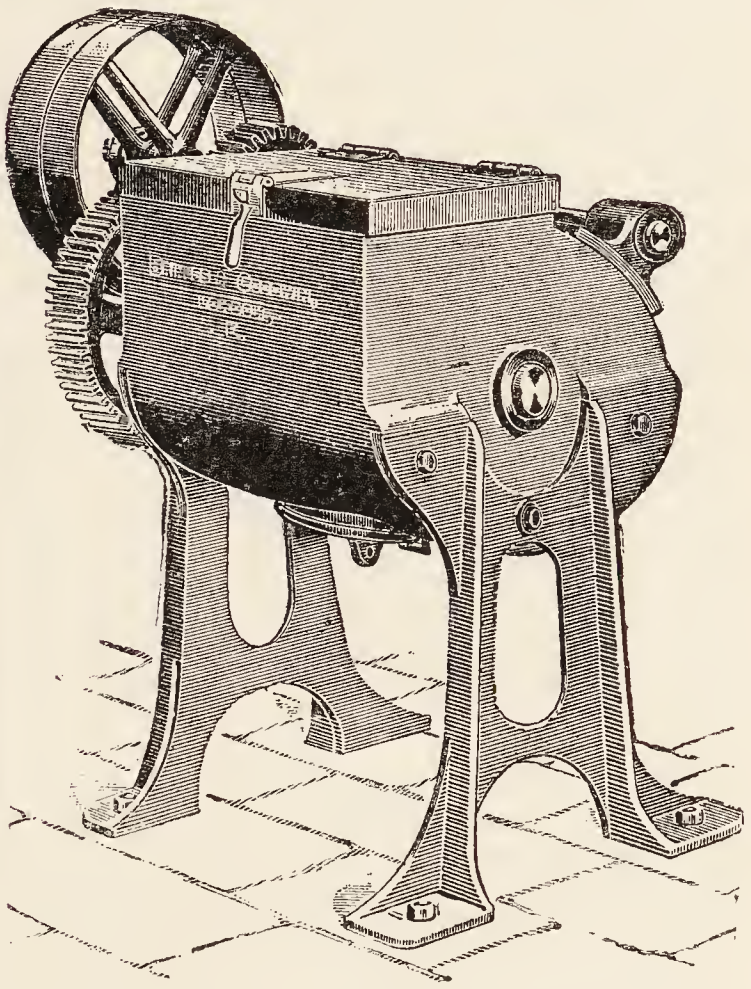


FIG. 10.

Geared Horizontal Mixer (Brinjes and Goodwin, Ltd.)

volatile medium be necessary, as in the production of enamels, a cone mill, Fig. 4, may conveniently be substituted.

The more important and widely used pigments, classified according to colour, will next be briefly described. For further details *v.* art. PIGMENTS.

WHITE PIGMENTS.

White Lead (*Céruse, Cerussa Alba, Blanc de Plomb, Krems white, Bleiweiss*). For manufacture *v. White lead*, art. LEAD.

Characters of good white lead.—A perfectly amorphous white pigment, possessing great opacity and fairly good stability, with the power of drying rapidly when mixed with linseed or a similar oil and exposed to the air. Its great popularity in paints is principally due to its power of combining to a certain extent with the oil medium used, the lead linoleate formed conferring certain physical properties of flow under

the brush, which are highly esteemed in practice, as well as a good degree of impermeability to moisture. The composition of white lead approximates to the formula $Pb(OH)_2PbCO_3$, which would represent 70 p.c. lead carbonate and 30 p.c. lead hydroxide, whilst the average number of samples contain approximately 72 p.c. of the former and 28 p.c. of the latter substance. It has a specific gravity 6·6, and an oil absorption as low as 6, in some samples. When ground in oil, lead hydroxide would alone give little opacity, which is imparted by the carbonate present; the latter forms an emulsion of extreme opacity with the oil. Both components, therefore, are essential. The production of white lead 'paste' or white lead in oil can be made either by grinding the dry pigment in oil or by 'pugging' or milling the wet pulp with linseed oil as it comes from the filter press. The superior affinity of white lead for oil drives out the water. White lead enters into the composition of many paints as 'base,' on account of its high opacity and comparative stability, and many pale-coloured tinted paints are obtained therefrom by the addition of a small proportion of stainers. Of all white pigments white lead has the greatest tendency to turn yellow in the dark, but the yellow shade is bleached on exposure to light. The pigment is easily blackened by sulphuretted hydrogen. On exposure to prolonged sunlight and weather white lead paints lose their gloss and chalk, *i.e.* the oil medium seems to disappear leaving the pigment in an unbound chalky condition, which is probably due to the catalytic action of lead as a drier continuing after the paint film has become dry. Too little attention has been paid to the value and the amount of the medium used in consideration of the stability of white lead in paints.

There has been much controversy on the prohibition of white lead in paints, owing to the danger of lead poisoning. Much work has been done in finding innocuous substitutes and where it is necessary to use white lead restrictions have been drawn up so as to protect the health of the workers. The probability of contracting the disease of lead poisoning may be reduced to a minimum by proper methods of hygienic control and by the abolition of dry rubbing down of a lead paint surface previous to repainting. For indoor work white lead is not essential, but no substitute for a white lead paint has been found which shows the same durability on exposure to the atmosphere. Regulations for the use of white lead or sulphate of lead in paint have been prepared by H.M. Home Office in collaboration with the Painters' and Decorators' Industrial Joint Council of Great Britain, to give effect to the resolutions passed at the International Labour Conference at Geneva, 1921.

Of the other white lead pigments the only one which has attained a moderate degree of popularity is the basic sulphate, which varies in lead oxide content of 1 p.c. or 2 p.c. up to 35 p.c. The usual method of manufacture is by sublimation of galena, PbS, in a current of air. No specific claim for distinction from white lead in properties seems to have been made, except the erroneous one of its absence of toxicity. It has, however, found extensive application as a constituent of paints in U.S.A. Reference to mixed lead and zinc white pigments will be made after the description of zinc white.

Zinc oxide or zinc white (*Chinese white*) is manufactured by the French process, consisting in burning metallic zinc in a current of air, or indirectly by burning zinc ore, the product differing from that of the French process by its lesser purity of composition and colour. Zinc oxide is the whitest of all commercial pigments and is most suitable for use in white enamel. Owing to the basic nature of zinc oxide care must be exercised in the selection of the medium, a badly refined oil of high acid value being unsuitable, because of the stiffening or 'livering' which occurs after grinding. The opacity of zinc oxide is equal to or possibly greater than white lead, but owing to its greater oil absorption (15 p.c. as against 6 p.c.) the opacity of a zinc white paint appears less than that of a white lead paint, on account of its lower pigmentation (H. Pfund, J. Franklin Inst., 1919, 188, 675). On the other hand, the spreading power or relative area covered by unit weight of zinc white paint is much greater than with white lead. The stability of zinc white in paint films is good. It is non-toxic, and not visibly affected by sulphuretted hydrogen. It can be used with oil or water media, and remains well suspended in oil paints. In an oil vehicle it dries far less rapidly than lead white. Zinc white paints do not crumble nor chalk but peel off finally in patches, whereas white lead crumbles with a fine network pattern over the surface. White lead and zinc oxide are in these properties complimentary, and in judicious admixture they produce a more perfect paint than when either constituent is used alone.

——	c.c. medium per gram pigment at painting consistency	Total pigment required	Relative hiding powers of equal masses of pigments	Relative opacities of paints of equal consistencies	Vol. of paint containing 1 gram of pigment
Lithopone .	0·61	2·0	100·0	100·0	0·85
Zinc oxide .	1·07	2·56	87·8	53·0	1·25
White lead .	0·42	3·88	51·6	77·0	0·57
Timonox 'green star' . .	0·57	2·34	85·4	95·5	0·76

Lithopone, Orr's white, Charlton white, or Beckton white.—One of the most interesting of white pigments, lithopone is quite unaffected by sulphuretted hydrogen and is the most opaque of all white pigments, whilst its staining or killing power is considerably greater than that of white lead, to which it is nearly equal in fineness or subdivision. It possesses little or no basicity, and can be used in the most acid media without fear of 'feeding.' It has a tendency to darken in sunlight, but many manufacturers produce a pigment that is fast.

Until recently standard white pigments have consisted of white lead, zinc oxide, basic lead sulphate, and lithopone; but pigments containing antimony oxide or titanium oxide are recognised as products meriting serious consideration.

Antimony oxide pigment results from the condensation of antimony oxide vapour produced by the roasting of antimony ores (Antox, Costerfield Mine, Australia). The colour varies from pure white to dull orange, depending on the temperature of working. The pigment, Timonox, has a specific gravity of 5·4, and produces a good paste when ground with 10 p.c. of oil. It has no accelerating effect as a drier, can be reduced with barytes or blended with zinc white; it is unaffected by ultra-violet light and by sulphides under average conditions. It is non-poisonous (H. E. Clarke, J. Oil and Col. Chem. Ass. 1921, 4, 2).

Titanium oxide is obtained from a variety of ilmenite (Egersund, Norway). The ore is freed from associated minerals, and the concentrate, containing 47·5 p.c. titanium oxide, is finely powdered and heated with concentrated sulphuric acid to give soluble sulphates of iron and titanium; the mass is extracted with water, and on heating the reduced solution to boiling titanic acid is precipitated. The acid is dried and calcined at a high temperature. In practice barium sulphate is mixed with the solution before precipitation, and a small amount of calcium phosphate and barium carbonate is added to the pulp before calcination. This addition has been found to produce a more uniform product. The composite product, titanium white, is 'extra' and 'standard,' the latter contains 75 p.c. barium sulphate and 25 p.c. titanium oxide. The pigment is non-toxic and unaffected by sulphuric acid and sulphuretted hydrogen. The paints show no tendency to crack and peel, and a combination of titanium white and zinc oxide is durable. The pigment possesses greater opacity and spreading power than any other white pigment (N. Heaton, Roy. Soc. Arts, 1922).

Fillers and extenders.—An inert filler, *e.g.* common whiting or barytes, is often used so that the physical properties of a paint may approach those of the more normal pigments, the quantity of colour pigment employed being merely sufficient to secure opacity and adequate pigmentation. The usual fillers are *Barytes and Blanc Fixe*, natural and artificial barium sulphate. The barytes must be carefully chosen, because the presence of traces of iron produces a yellow shade after the pigment is rubbed with linseed oil. The inactivity of barytes, its low oil absorption value (6–9), and its high sp.gr. (4·2–4·5), makes it an important diluent of paints, and it is used in the trade to dilute white lead. Although primarily an adulterant the crystalline nature of the particles affords a good surface for repainting, whilst films containing barytes suffer less contraction than is the case when pure white lead is used as a pigment. It possesses little opacity and is deficient in 'killing' power, so that pigments, *e.g.* greens, can be reduced with barytes with little loss of purity of colour. Blanc fixe has a greater oil absorption and higher opacity than barytes. Blanc fixe finds principal application in serving as a base for the striking of dyes to lakes and in the reduction of pure strong colours such as ultramarine and Prussian blues, when the light reflecting power or visibility of hue becomes apparent without manifestation of undertone or production of 'muddiness.' *Strontian white* is of limited occurrence although possessing similar properties. *Whiting* [*Paris white* (*Gilders' whiting*), *Precipitated chalk*, *Barytes substitute*] consists of ground and levigated chalk, but it is little used as a pigment because of its low opacity, whilst its high oil absorption (15 p.c.) does not make it economical for use as a filler. When ground with linseed oil (18 p.c.) it gives putty. It forms a valuable pigment in water paints, where it appears to function as a pigment of high opacity. It is not safe to mix it with pigments which are altered by alkalies, *e.g.* Prussian blue, because of the presence of traces of quicklime. Precipitated chalk, barytes substitute, is a by-product from the process of water softening, and was largely used during the War as a substitute for barytes. It is decidedly crystalline in structure, with rather lower oil absorption and better colour than the natural article. Gypsum is used largely by paper-stainers and makers of paper hangings, who prefer it to barytes because of its better 'body.' It has no 'body' in oil and can only be used as an adulterant. *Alumina*—precipitated alumina is very transparent when mixed with oil, so that it finds no application in paint pigments, but it is widely used as a base for transparent lakes or in printing inks where great transparency is desired. *China clay, Devonshire clay, Kaolin*—. China clay is a hydrated aluminium silicate

$$Al_2O_3 2SiO_2 2H_2O$$

and is a disintegration product of granite. On account of its high oil absorption and transparency it is of little value as a pigment in oil paints, but it remains in good suspension in oil and inhibits the settling of other pigments, red lead, barytes, &c. It is largely used as a base for the precipitation of coal-tar colours intended for use in transparent oil pigments for printing inks or water paints, and is the main pigment in water paints or distempers. Its function as an electro-negative colloid in aqueous media, the stability of suspension of which is increased in the presence of alkalies, makes China clay an ideal pigment. *Asbestine*—asbestos as a fine white powder gives 'tooth' to other pigments, and is used as an adulterant in cheap paints. It has no body, is coarser in texture than barytes, gritty to the touch, and when ground in oil acquires a muddy colour due to impurities.

Silica.—Although this substance can hardly be classed as a pigment, it enters largely into the composition of many types of paints, owing to its crystalline structure giving 'tooth' to an otherwise smooth or soapy pigment. It is largely used as a wood filler. Silica has no opacity when mixed with oil, and its oil absorption varies with its fineness of division.

Yellow Pigments.

Yellow ochres, Terra di Siena, Stone yellow, Roman yellow, Mineral yellow, Oxford ochre, Golden ochre, &c. Argillaceous earths, containing varying percentages of hydrated ferric oxide, form very durable and trustworthy pigments. Their tone, opacity, and staining powers vary considerably in a manner independent of their composition. The process of manufacture consists of crushing, levigation, and drying. The palest varieties are found in France, but they possess little opacity. The most valuable

staining ochres come from the neighbourhood of Siena, from which certain varieties yield tints resembling yellow ochres on reduction. The Irish and South American ochres possess high staining powers of somewhat dull colour. Their large content of manganese (0·5–4·0 p.c.) renders their use in high-class paints and enamels somewhat dangerous, on account of the progressive oxidising effect conferred on the medium. *Mars yellow* is an artificial preparation of similar composition. A pigment called by the same name, also termed *Siderin yellow*, is $Fe_2(CrO_4)_3$. *Chrome yellow* is $PbCrO_4$: also $PbCrO_4 \cdot PbSO_4$; and $PbCrO_4 \cdot 2PbSO_4$. Pale and greenish shades contain citrate or tartrate of lead, and sometimes also sulphate, as well as lead chromate. *Orange chrome yellow* is $PbCrO_4 \cdot PbO$. *Cologne yellow* is $PbCrO_4$, $PbSO_4$, and $CaSO_4$. In the preparation of the different tones of chromes—primrose, lemon, middle, and orange, Derby, Persian, and Chinese reds, the redder tones of chromes are obtained by increasing the basicity of the product. The yellow and orange chromes are the most important of the yellow pigments, having a high opacity and staining power; they are fast to light and fairly stable to acid fumes, but are affected by sulphuretted hydrogen. The lead chromes are used in the manufacture of green pigments in combination with Prussian blue. They are not used in distemper paints, because of the tendency of the free alkali to impart a reddish hue. *Barium*, *Strontium*, and *Zinc yellows* ($BaCrO_4$, $SrCrO_4$, and $3ZnCrO_4, K_2CrO_4$) have a poor staining power and low opacity, but zinc chromate gives a beautiful green with Prussian blue, the distinction from lead chrome green being probably based on its relatively higher staining power than transparency. Barium chromate (*lemon yellow*, *yellow ultramarine*) is stable to sulphuretted hydrogen. *Bismuth yellow*, also a chromate (not permanent). *Cadmium yellow*, CdS, durable, of fairly good body, and unaffected by sulphuretted hydrogen. True *Naples yellow*, antimoniate of lead (permanent in oil). Cadmium sulphide, and a pale yellow ochre, have been sold under the same name. *Montpellier*, *Cassel* ($PbCl_2.7PbO$), *Turner's*, *Turnin*, *Verona*, and *Paris yellows*, oxychlorides of lead (not lasting). *King's yellow* or *Orpiment*, As_2S_3 (unstable). *Wolfram*, *Vanadium*, *Uranium*, *Thallium*, *Palladium*, *Tin*, *Antimony*, and *Platinum yellows* (most unstable and little used). *Indian yellow* or *Purree*, impure magnesium euxanthate, $C_{19}H_{16}MgO_{11}, 5H_2O$, prepared from the urine of cows fed on mango-leaves. A beautiful but variable pigment. *Madder yellow*, *Italian pink*, *Brown pink*, &c. (vegetable: non-durable—bleached on exposure). *Gamboge* (a vegetable resin; unstable). *Aureolin*, occasionally called *Cobalt* or *Indian yellow*, potassium cobaltinitrite, $K_6Co_2(NO_2)_{12}, xH_2O$ (fairly permanent).

Yellow pigments from coal-tar dyes are of small importance in the paint industry, on account of their poor opacity. They are derived from monoazo-dyes, of which Hansa yellow is a well-known type. On account of their stability to alkalies they are used in distempers.

Red Pigments.

Vermilion, *Cinnabar*, HgS, is moderately permanent in oil, but unstable in water colour. It is too expensive for use in ordinary paints, except for certain special purposes where brightness and opacity are desired. *Minium*, *Red lead* (Pb_3O_4 or $PbO.Pb_3O_4$) is rarely used alone as a pigment, its main application being that of an addition to white lead or priming paint. *Light red*, calcined yellow ochre; *Indian reds* are characterised by a high degree of opacity and staining power. Owing to their careful preparation they are finely divided pigments and are employed in high-class work. Indian red was the name originally given to a very pure form of red oxide found in India, but it is now applied to iron oxides produced by calcination of iron liquors. Three varieties—light, middle, and deep—are recognised in the trade.

Spanish red oxide is a naturally occurring iron oxide. Its use is restricted to coarse red paints for the protection of metal work, and where fineness is not of importance it is considered to be a powerful preventative of rust. *Venetian red* is the name usually applied to artificially prepared iron oxides produced by heating precipitates obtained by the interaction of ferrous sulphate with slaked lime. It has a brighter colour than light Indian red, and possesses a staining power and opacity roughly proportional to its iron oxide content. Barytes is sometimes added to reduce the cost. *Turkey red*, *Scarlet red*, *Rouge*, *Colcothar*, *Bole*, *Caput mortuum*, are the purest form of bright oxide of iron obtained by calcination. The red oxides are permanent to light and most chemical agencies. When the artificial varieties are carefully prepared they are very inactive to the medium. The presence of traces of sulphuric acid is deleterious, and often explains the retardation of drying which occurs in paints containing them. *Chrome red*, *Austrian cinnabar*, *Derby red*, *Persian red*, or *American vermilion* are basic lead chromates reverting to orange and yellow pigments by loss of their crystalline structure on grinding. They are comparatively unimportant as red pigments. *Realgar*, As_2S_2, arsenic sulphide. *Antimony vermilion*, antimony sulphide, Sb_2S_3. *Palladium red*, ammonio-chloride of palladium, and *Brilliant scarlet*, mercuric iodide (very unstable), have been used. *Vandyke red* is copper ferrocyanide, $Cu_2Fe(CN)_6$. The cobalt reds are too costly for general use. *Madder* lakes (vegetable colours on mineral bases; unreliable). *Carmine lake* (of animal origin—from *Coccus cacti*; a beautiful colour, but not permanent). Red pigments from coal-tar dyes are produced by precipitation or 'striking' of a water soluble dye on a base consisting of blanc fixe, white lead, lead sulphate, orange lead, &c., by means of a mordant. The lakes (*v.* Art. on Lakes) derived from monoazo dyes are more numerous and important from the point of view of pigments. The dyes consist of a 'coupling' product obtained by combination of a diazotised amine with a phenol, naphthol, amine, or derivatives of the same. Two of the most important dyes for the preparation of bright red lake pigment are Lithol red B. and Paranitraniline red, which are respectively sulphonaphthaleneazo-β-naphthol and *p*-nitrobenzeneazo-β-naphthol; the former is perhaps the most important red lake pigment used in the paint trade, and is characterised by

great fastness and insolubility in oil (non-bleeding). The paranitraniline reds, although fast to light and brilliant, are liable to bleeding. Other important pigments are obtained from dyes, of which the naphthol sulphonic acids are the starting points. *Helio fast red R.L.* (toluidine toner), a derivative of *m*-nitroparatoluidine, 1 : 3 : 4, is an important lake-producing dyestuff, and is one of the fastest to light (Allsebrook, Proc. Oil and Col. Chem. Ass., 1919, 2, 14). *Madder* or *alizarine lake* is obtained by combination of an alizarine dyestuff with aluminium hydrate. It forms a deep red somewhat transparent pigment with a fine blue undertone, and is useful in obtaining shades of maroon and purple. It is very fast to light, but is apt to retard drying of the medium.

The *eosine lakes* or *vermilionettes* are prepared by precipitating derivatives of fluorescein with lead or aluminium salts. Although of very bright shade they are very fugitive to light, and it is the practice to reduce this fugitiveness by precipitating the lakes on lead bases, *e.g.* white lead, lead sulphate, or orange lead. They are being gradually replaced by the more permanent naphthylamine reds (Jennison, Manufacture of Lake Pigments from Artificial Colours). The Badische Anilin und Soda Fabrik (J. Soc. Chem. Ind., 1917, 639) have patented a process for the manufacture of a bright red pigment insoluble in water and oil, very fast to light and not affected by water or lime; the diazo-compound of 1-aminoanthraquinone is combined with 1-benzoylaminohydroxynaphthalene with or without the addition of Turkey red oil.

Green Pigments.

Terre verte, an impure ferric silicate, has been used as a pigment from very early times, being one of the best permanent greens available to the early painters. Bohemian or Veronese earth (Green Earth) occurs native as augite, consisting of a hydrated silicate of magnesium and aluminium containing small amounts of iron. The bulk of the green earth is mined in Germany, but a certain amount is found in this country. It has a dull green colour with small opacity or staining power. It is very fine in texture and is used in modern lime colours, owing to its capacity for fixing basic coal-tar colours to a certain extent without the aid of precipitants, and so firmly, that the resulting colours are quite proof against the alkaline action of quicklime. Many salts of copper have been used as green pigments. Among the best known of the copper greens are *Malachite*, *Mountain green*, or *Green verditer*, hydroxycarbonate of copper, $CuCO_3,CuH_2O_2$, *Schweinfurt*, *Paris or Emerald green* (acetoarsenite)

$$3(CuAs_2O_4)\cdot Cu(C_2H_3O_2)_2$$

Brunswick green (oxychloride), $CuCl_2\cdot 3CuO,4H_2O$, and *Verdigris* (basic acetate)

$$2Cu(C_2H_3O_2)_2,CuO,6H_2O$$

Scheele's green is a basic arsenite of copper, now but little used. *Mitis*, *Vienna*, and *Kirchberger greens* have the same composition. *Bremen green*, *Green ashes*, *Elsner green*, *Gentele's green* (stannate), and *Mineral green*, are other copper pigments. All are darkened by sulphuretted hydrogen, and most are very poisonous.

Malachite greens (Malachite green, zinc double chloride of tetramethyl-*p*-amidotriphenyl carbinol) combine with green earth directly, giving fast shades to light, alkalies, and are non-bleeding. As the preparation of the green earth is improving, so are the pigments derived from them in the properties mentioned.

The green lakes have not found any extensive application in the paint industry on account of the superiority of the Brunswick greens. Lakes from malachite green, naphthol green, &c., struck on green earth are used in distempers, on account of the non-resistance to alkali of the Prussian blue in Brunswick green.

Brunswick greens are made in several tints—light, middle, deep, and extra deep—and consist of a mixture of Prussian blue and chrome yellow. The cheaper varieties are made by reducing with barytes. Chrome yellow when replaced by zinc chromate yields a green of fine quality, which when combined with yellow ochres or umber yields a series of fine olive greens.

Brunswick greens are pigments of high staining power and good opacity, and combine the properties of their two constituents. They must not be confounded with the pigment of the same name, which is a compound of copper, and is now hardly ever used.

Chromium, *Guignet's*, *Pannetier's*, *Arnaudon's*, *Plessy's*, and *Chrome emerald greens* are hydrated sesquioxides of chromium, with phosphate or borate of chromium. *Guignet's green* is used as a pigment for india-rubber, as it withstands the temperature of vulcanisation and the action of sulphur without losing its colour. It is very fast to light and chemical agencies, but it is of too poor a body and too dull in colour to commend itself for use as a paint pigment. *Virdian* is $Cr_2O_3,2H_2O$ (*v.* Chromium). Other chromium greens are Casali's, Dingler's, and Schnitzer's products. *Rinmann's green*, *Cobalt green*, or *Zinc green*, a compound of oxide of cobalt and oxide of zinc. *Titanium*, *Vanadium*, *Uranium*, *Manganese*, *and Molybdenum greens* are also occasionally met with as pigments. *Green ultramarine* is a calcination-product in the manufacture of artificial ultramarine. There are many unstable green lakes of vegetable origin, such as *Chinese green*, *Iris green*, and *Sap green*, but they are of little or no value.

Blue Pigments.

Prussian blue, *Berlin blue*, *Chinese blue*, *Paris blue*, *Antwerp blue*, *Milori blue* represent varieties differing only slightly in shade. Prussian and Chinese blues are the best known varieties in the trade. Brunswick blue is a reduced Prussian blue, *i.e.* a mixture of Prussian blue and barytes. Chinese blue, or bronze blue, is considered the finest of this class of pigments, and is distinguished by its bronze cast, which causes it to find favour in printing inks. The generic term Prussian blue characterises pigments composed of basic iron in combination with ferrocyanogen and ferricyanogen. They are pigments of high degree of staining power with little opacity. Fairly fast to light they have the curious property of bleaching on exposure to strong light and regaining their colour in the dark. Although they resist the action of acid fumes they are readily decomposed

by alkalies, therefore they must not be used in combination with pigments liable to contain alkaline material, *e.g.* whiting or China clay, and they are inadmissible as pigments in distempers. A small but definite proportion of adsorbed alkali forms an integral part of Prussian blues, and the substitution of sodium for potassium gives pigments inferior to those from the potassium salt in the beauty of their tones. *Indigo*, or *Indigotin*, $C_{16}H_{10}N_2O_2$ (vegetable: fades on exposure). *Native ultramarine*, pulverised lapis lazuli (an excellent and stable but costly colour). *Artificial ultramarine*, probably $Na_4(NaS_3Al)Al_2(SiO_4)_3$ (Brögger and Backström), a compound of silicate of aluminium and sodium, with sulphide of sodium; suggested by Gmelin, in 1827, and made by Guimet in 1828. Less expensive than native ultramarine, and nearly equal to it as a pigment. *Ultramarine* is a pigment of bright blue colour, which varies from a greenish-blue to a deep bluish-violet. It does not possess great opacity, is not so strong in staining as Prussian blue. It is fast to light and alkali, but both native and artificial ultramarine are immediately bleached by acids (*v.* ULTRAMARINE). *Thenard's blue*, phosphate and aluminate of cobalt. *Cobalt blue*, *Ghan's ultramarine*, *Azure blue*, aluminate of cobalt. *Cobalt blue* has a pure blue tint with a tendency to appear slightly violet in artificial light. It is quite permanent when exposed to light and air, and is unacted on by acids and alkalies. It is too expensive for general use in painting, but it is largely used by artists, especially as a water colour, as it works better in water than in oil. *Cyanine*, *Leitch's blue*, a mixture of cobalt blue and Prussian blue. *Smalt*, *Zaffre*, *Royal*, and *Saxony blues*, glasses coloured by cobalt oxide. *Smalt*, *Cœruleum* or *Egyptian blue*, was originally an artificial silicate of copper and soda. In mediæval times it was known as Smaltine and the copper was replaced by cobalt and the soda by potash. *Cerulean blue* $3(SnO_2,CoO)+SnO_2$ (stannate of cobalt). The cobalt colours lack somewhat in body and permanency. *Copper blues*, carbonates, silicates, and other salts of copper, are of little value. At one time the copper blues were largely used for painting of all kinds, but like smalt they have been superseded by Prussian blues and ultramarine.

BROWN PIGMENTS.

Vandyke, *Rubens*, *Cassel*, *Ulmin*, and *Cologne browns*: some of these are partly vegetable, and are prepared from peat, cotton, soot, &c.; bituminous matter is often present. Several different pigments are known as *Vandyke brown*. Only those prepared by calcining highly ferruginous brown ochres, or consisting of a dark-tinted form of colcothar, are permanent. The variety of Vandyke brown, consisting of a bituminous earth, is far less durable. *Vandyke brown* is not fast to light and is so transparent that its use is entirely restricted to that of a stainer. It is used when ground with either water or oil for conferring a walnut colour to wood. *Raw* and *Burnt sienna*, *Brown terre verte*, *Raw* and *burnt umber*, *Cappagh brown*, and *Mars brown*, are earths or ochres, raw or calcined. *Raw sienna* resembles yellow ochre in composition, but does not possess the same opacity, whilst its staining power is higher. Burnt sienna is obtained by the calcination of the raw variety. Raw and burnt umbers are distinguished as Turkey umbers and English umbers, the former being mined in Cyprus and are valued on account of their strength and purity of colour. In composition they resemble manganiferous ochres with a manganese content in some cases as high as 20 p.c., which requires that they must be used with caution. Crude unground umber is used by the oil boiler as a drier for dark-coloured oils, both iron and manganese passing into solution in the oil. Most of the umbers are durable and reliable pigments. Other browns are *Prussian brown*, made by calcining Prussian blue; *Madder brown* (of vegetable origin, and liable to fade); *Bistre*, a bituminous brown; *Asphaltum*; and *Mummy*. The last three also are untrustworthy and fugitive.

BLACK PIGMENTS.

The black pigments used by the painter are with one exception varieties of carbon black obtained by burning organic substances in an insufficient supply of oxygen. Gas black is a crude form of carbon obtained as a by-product in gas works, but it is of little use in paints. Lamp black and Vegetable black are obtained by incomplete combustion of various oils in specially constructed chambers. The finest variety, vegetable black, is relatively free from oily products which exercise a retarding action on the drying of paint. Lamp black is a permanent pigment of high opacity and staining power. On reduction with white pigment it gives cold greys. Drop black or Frankfort black is made from vine twigs, ivory cuttings, bone shavings and other organic materials, which are calcined until complete charring is effected. After grinding the black so obtained is made up with glue and water into pear-shaped drops. Ivory black and bone black are obtained by distillation of bone material. Ivory black is a black of very intense colour, but is little used as a staining pigment. Carbon black is formed by the ignition of American natural gas in a regulated supply of air. It is the purest form of carbon pigment known (95–99 p.c. purity). It possesses high staining power and opacity, but it differs from lamp black in giving warm browns on reduction with white pigments. It is of very fine texture and works well either in oil or water, being devoid of oily or aqueous impurity. It is used for the manufacture of high-class black enamels.

Indian ink consists of very fine lamp black, together with gelatine and a perfume (*v.* INDIAN INK). Black oxide of iron, Fe_3O_4, is a naturally occurring pigment found in ochre deposits in England. While it possesses neither the transparency not the staining power of carbon blacks, it finds application in paints on account of its comparatively low oil absorption (about 30 p.c.).

As regards durability of the above pigments, it may be shortly stated that all the compounds of copper, lead, and bismuth, and some mercurial pigments, darken more or less when exposed to air containing sulphuretted hydrogen. Most of the colours which are partly or entirely of organic origin fade on exposure, by a process of

oxidation. On the other hand, pigments which are not affected by foul gases, the barium and zinc whites, for example, have unfortunately, for the most part, less covering power than the majority of lead, copper, and other changeable pigments. Many of the defects of painting may be prevented by using paints of a composite class based upon white lead pigments, containing sufficient zinc-oxide (25–50 p.c.) to present a fine hard film. Great circumspection must, therefore, be exercised in the choice of a pigment, whether for artistic or ordinary work. As a rule, pigments are less fugitive in oil-media then when mixed with the usual water-colour vehicles. Church (The Chemistry of Paints and Painting, 1901) classifies artists' pigments, according to their stability in oils, as shown in the following table:

Class I. Truly permanent.	Class II. Somewhat changeable.	Class III. Untrustworthy.
Baryta white.	Aureolin.	King's yellow.
Zinc ,,	Baryta yellow.	Yellow madder.
× Flake ,,	Indian ,,	Brown pink; yellow lake.
Yellow ochre.	Strontia ,,	Gamboge.
Raw sienna.	× Chrome ,,	Zinc chromate.
× Naples yellow, true.	Madder carmine.	Crimson lake.
× Cadmium ,,	Rubens' madder.	Carmine and burnt carmine.
Cadmium orange.	Rose ,,	Indian lake.
× Vermilion, artificial.	Madder red.	Scarlet ,,
Vermilion, native.	Purple madder.	Purple ,,
Indian red.	Mars violet.	Violet carmine.
Light ,,	Emerald green (Schweinfurt g.)	Verdigris.
Venetian red.	Terre verte.	Sap green.
Red ochre.	× Malachite.	Green vermilion, etc.
Cobalt violet.	Smalt.	Indigo.
Manganese violet.	Prussian blue.	Blue verditer.
Viridian (emerald oxide of chromium, $Cr_2O_3,2H_2O$).	Antwerp ,,	Blue ochre.
	× Madder brown.	Bituminous Vandyke brown.
Green oxide of chromiun, Cr_2O_3.	Cologne earth.	
Cobalt green.	Bitumen.	
Green Ultramarine.	Earthy Vandyke brown.	
Ultramarine.		
Artificial ultramarine.		
Cobalt.		
Cœruleum.		
Burnt sienna.		
Raw and burnt umber.		
Cappagh brown.		
Verona ,,		
Prussian ,,		
Ivory black.		
Charcoal black		
Lamp-black.		
Graphite.		

To adapt this table to water colours, the pigments marked × must be relegated to class III.; while Indian ink, bistre, and sepia may be added to the table, but the two last named must be placed in class III.

The following examples of carefully chosen palettes are quoted from Church's work, just cited: (*a*) for *oil-painting*, flake white, yellow ochre, cadmium yellow, aureolin, vermilion, madder carmine, ultramarine, viridian, Cappagh brown, and ivory black: (*b*) for *water-colours*, Chinese white, yellow ochre, cadmium yellow, aureolin, red ochre, madder carmine, ultramarine, viridian, Mars brown, and Indian ink.

Of the work of painters of pictures in the first half of the nineteenth century, two types from different schools, from the artistic point of view, have stood best the test of time, viz. those of the pre-Raphaelites and those of W. P. Frith. In 1860 Holman Hunt made continuous experiments on pigments and media, and A. P. Laurie, in 1922, has published the results of the examination of Holman Hunt's experimental canvases. The general conclusion was that the accepted list of permanent pigments as used to-day is reliable with two exceptions, viz. cobalt yellow in oil and pale cadmium yellow, whilst chrome yellow when properly protected might be included on the artist's palette.

The darkening of the oil is due to the presence of lead driers. No lead driers should be used for artists' purposes. In many cases copal varnish had been mixed in as a medium, but there was no indication that the colours had been preserved better by this treatment. The present practice of protection by an easily removed mastic varnish is justified.

Media or **Vehicles.** *Definition.*—The fluids or other materials with which pigments are intimately mixed for the production of paints. For *oil-paints*, the vegetable drying or siccative oils

are employed, and for *water-colour paints*, size, honey, glycerol, and aqueous solutions of gums, or the like, are in use. Oil of turpentine is frequently added to the oil medium, acting partly as a 'thinning' agent, and partly to accelerate somewhat the drying of the paint. Benzene, and turpentine substitutes, allied to petroleum spirit, are similarly used. In *tempera-painting* albuminous or gelatinous media are employed, and water-glass is the vehicle in *stereochromy*. Lime-water or baryta-water is used in *buon*, *fresco*, and *fresco-secco* painting. In *pastel painting*, the bases for the pigments are whiting, and (sometimes) plaster of Paris, or kaolin. Beeswax was the medium in Greek and Egyptian *encaustic* work, and is employed in *spirit-fresco*. Other paint-media are occasionally made use of, and will be referred to presently.

Oils. These are chosen for their drying properties, or, in other words, their power of absorbing oxygen when spread in thin layers and exposed to the atmosphere; by this oxidation a film of a drying oil gradually becomes converted into a coherent coating of a hard, elastic, varnish-like substance.

Linseed oil is the most important and commonly used drying oil; it is met with in commerce under the names of *raw*, *refined*, *artists'*, and *boiled* oil. Raw oil is as expressed from the seeds. By agitation in lead-lined tanks with 1 p.c. of strong sulphuric acid, boiling with water or treatment with steam, and drawing off in settling-tanks from water and sediment, raw oil is converted into refined oil. Artists' linseed oil has been allowed to stand for weeks or months, then treated with litharge and finally bleached by exposure. Other processes of refining are also used. Boiled oil has been heated in air to 130°, or thereabouts, and maintained at that temperature for a little while. Raw linseed oil possesses great drying powers, which are considerably enhanced by the operation of boiling. Boiled oil is therefore a most important article to the painter. M. Toch is of the opinion that spar varnishes and varnishes made with thickened linseed oil, or with open kettle boiled oil, are the best paint vehicles as protective agents against corrosion. H. A. Gardner confirms Toch's views, and recommends that a protective coating of paint for iron in cement and concrete structures should contain a vehicle of boiled oil or an oil drying by polymerisation with a coarse pigment of the basic or chromate type to induce passivity of the metal. Ahrens prefers heated China wood oil as a vehicle. An excellent report on the testing of paint vehicles (China wood oils) is issued by the American Society for Testing Materials (1915). The drying power of boiled oil is still greater if litharge or some other drier has been added during the operation of boiling. The drier appears to act as a carrier of oxygen to the oil, and compounds of the metallic oxide with the linolenic and linolic acids is stated to be formed (*v.* Oils, Fixed, and Fats; Driers). Both raw and boiled linseed oil are used in the manufacture of ordinary paints, while for the more delicate colours employed in the fine arts, refined and artists' oils are preferred.

Poppy, walnut, hempseed, and castor oils are also used in the manufacture of paints, especially the first three. These oils are, however, almost exclusively used by artists; and linseed oil holds its own as the most generally useful and applicable drying oil. Numerous additions to, and substitutes for linseed oil have been tried, among them mineral and resin oils, China wood oil (Tung oil), Nigerseed oil, cotton-seed oil, menhaden oil, and marine animal oils.

Artists in oil generally use media which contain copal, amber, or some other resinous varnish, and a diluent, such as turpentine, in addition to the drying oil. A good artists' medium can be prepared by gently warming a mixture of linseed or poppy oil with strong copal varnish and a trace of bleached beeswax. A less satisfactory medium is 'megilp,' composed of linseed oil and mastic varnish. Such media are added to the mixed colours by the artist.

The vehicles for water-colour paints need no description; they are, chiefly, isinglass, size, gum-water (gum-arabic, gum-tragacanth, and gum-senegal are all used), honey, dextrin, and glycerol. Dextrin is less adhesive and less brittle than gum. An alcoholic solution of honey-lævulose is preferable to honey itself.

The various 'pastes,' 'fritts,' and 'glazes,' used for ceramic ware, enamels, painted glass, and the like, are outside the scope of this article (*v.* Fritts and Glazes; Pottery).

Driers or **Siccatives.** The effect of these on the drying oils has been referred to. The driers mostly employed are litharge, acetate of lead, resinates of manganese and lead and cobalt, manganese dioxide, and manganous borate, manganese and cobalt linoleates. 'Terebines' or 'liquid driers' are solutions of certain of the above-named metallic organic compounds in linseed oil and turpentine. White lead itself has considerable siccative power; this is one reason why it is so especially useful a pigment. The 'driers' of house-painters are commonly sold ready ground up with boiled oil. They must be used with care, as they sometimes detract from the delicacy of the colour with which they are mixed; and for this reason the use of driers should be avoided as much as possible in paints intended for 'finishing coats.'

Patent driers consist of the driers mentioned above reduced with inert material, *e.g.* Paris white, barytes, whiting. The object of the reduction is to prevent the addition of excess of drier, as the amount must not exceed 1–2 p.c. of the paint. The reduced driers are ground in boiled oil or in varnish and oil foots. *Zumatic drier* consists of 25 lbs. zinc oxide, with 1 lb. manganese borate, and 1 lb. is used for 25 lbs. of paint. *Guyemer's drier* contains zinc oxide 980 parts, with sulphate of manganese $6\frac{1}{2}$ parts, zinc sulphate $6\frac{1}{2}$ parts, and manganese acetate $6\frac{1}{2}$ parts. Between 2–3 p.c. is sufficient for a paint.

Paints. Common oil-paints consist of pigments ground with oil in the paint mill to a thick paste, and mixed with 'driers.'

White paints. A white paint may consist of a white pigment or a mixture of white pigments, raw or boiled linseed oil, drier, and volatile thinner. The addition of 'inert' pigments other then in a proportion necessary to give 'tooth' must be looked upon as an adulteration.

Too small a proportion of oil will cause deficiency of flow, whereas too much oil results in poorness of body. The addition of thinner regulates the thickness of the film, and the proportion of drier depends on the properties of the pigment and the requirements of the paint. 'Tinted' white pigments, *i.e.* pale tints, are prepared by addition of the tinting pigments ground in paste form to the ready mixed paint.

Red and Brown paints. Bright red paints, *e.g.* Post Office red, Signal red, Cardinal red, are red lake pigments struck on a transparent base, blanc fixe, alumina, &c., and although of high staining power they possess little opacity. The opacity may be increased by precipitation of the dye on a base of high opacity, *e.g.* orange lead, white lead, or lead sulphate, or by precipitation on a transparent with a proportion of inert filler such as blanc fixe to prevent alteration of tone. The production of satisfactory paint and enamel product of bright red colour is difficult, owing to the unsatisfactory nature of the dyes available, but the natural and artificial earth oxides offer a wide range of products for the production of paints and enamels of a high degree of fastness to light and of good opacity. The staining power of Turkey red is so great that an inert filler is required as a reducer. Intermediate shades of maroon, purple, brown, &c., are obtained by combination of lake red with pigments. The naturally occurring and artificially prepared oxides of iron, containing 10 p.c. and upwards of Fe_2O_3, form the basis of the iron oxide paints for the protection of iron structures. The addition of basic lead chromate (American vermilion), zinc chromate, red lead, and zinc oxide renders these paints rust inhibitory.

Yellow paints. The bright yellow paints are almost exclusively prepared from lead chromates, which are commonly reduced with inert pigments, owing to their unnecessary thickness of coating applied and their high opacity. They possess good permanency except in the presence of acid fumes and are usually good driers. The naturally occurring ochres provide a wide range of pigments for the production of paints and enamels of a more subdued yellow than the lead chromates. The yellow ochres represent perhaps the most permanent of pigments, and some varieties possess high staining powers and opacity, moreover the tones obtained by their reduction with pigments of high opacity match closely those obtained from chrome yellows.

Green paints.—The various shades of green paints are obtained by a combination of blue and yellow pigments. The brighter shades are obtained by combination of lead chromates and Prussian blues. Greens made on such a basis (Brunswick greens) are fairly fast to light. The duller shades of green, viz. olive green and bronze green, are obtained by substitution of chromates of zinc or barium in the first case and by bright yellow ochres in the second, in place of lead chromate. Emerald green and oxide of chromium find a very restricted application.

Blue paints. The colour of these paints is generally obtained from ultramarine and Prussian blue. Neither pigment possesses high opacity, and it is customary to obtain satisfactory coatings by reduction with inert transparent fillers. There is a wide range of tones, from a greyish-blue to a reddish-purple with ultramarine, and a greenish-blue to a bronze-blue with the ferrocyanogen blues. Paints containing much ultramarine are bad driers, whereas ferrocyanogen blues are quite satisfactory in this respect.

Black paints. Black pigments all possess comparatively high staining power besides considerable opacity, so that it is inexpedient to employ them as sole pigments in paints. It is possible to incorporate opaque pigments such as white lead. In enamels care must be taken in the selection of the black pigment, because adsorbed oily impurities in lamp-black have an adverse effect on the flow and drying properties. The paints described above are ready mixed, of a consistency for direct application, and containing the necessary driers. Large users of paints generally purchase the material in the state of a stiff paste, which is thinned down with oil and thinners and the necessary driers added. Paint in the ordinary paste form is unsuitable for producing a flat drying surface, as the proportion of oil present is in excess of that which would give a matt surface. The paste paints are produced in a grinding medium, consisting of gold size and volatile thinner. Such paints are known as turps colours, ready-bound colours, or colours ground in turpentine. Owing to their deficiency in non-valatile binding medium care must be taken that undue evaporation does not occur, because difficulty would be experienced in afterwards diluting the paint to a thin consistency. Distemper painting, for absorbent surfaces, such as plaster, necessitates the application of a 'priming,' consisting of white lead, or, very commonly, whiting, ground in water and mixed with size. There is little to specify in reference to artists' oil-paints, excepting that they consist, or should consist, of *pure* pigments very finely ground in, and intimately mixed with, oil of the best quality, no base, such as white lead, being present. The proportion of oil used varies with the pigment, and ranges from less than 20 parts per 100 of pigment, for materials such as lead and zinc whites, to over 175 parts per 100 for colours such as raw sienna, burnt sienna, and the like. Artists' water-colour paints are met with in the forms of cakes, pastilles, and tube colours. Cakes and pastille colours are usually made by grinding the pigments into a paste with a mixture of isinglass, size, and gum-water; the paste is then compressed and dried at a moderate temperature. Such paints are ground on the palette with water before use. Tube or moist colours consist of the pigments made into a cream with honey, glycerol, &c. Glycerol is preferable to honey.

Many other kinds of paints besides those already mentioned are manufactured at the present time. The principal of these are the luminous, fireproof, damp-resisting, anti-corrosive, water, washable, and enamel paints; their composition is very varied, and only a few short notes can be included in reference to them.

Luminous paints contain phosphorescent sulphur-compounds of strontium, barium, or calcium, sometimes associated with bismuth, uranium, and other salts. The mixtures are submitted to a calcination process, and combined with suitable pigments and media.

Balmain's, Vanino's, Mourel's, and Lennord's luminous paints are well-known preparations belonging to this class of paints. Calcium tungstate is stated to yield an especially powerfully phosphorescent product.

Fire-proof paints. These paints differ widely in composition, but asbestos is present in nearly all; and many contain alkaline silicates, borax, ground fluorspar, glass, and similar substances. A mixture of aluminium and sodium silicates is sold under the name of 'fireproof cyanite.'

Water-proof or **Damp-resisting paints.** Lime, crushed flint and marble, sawdust, shellac, asphaltum, gutta-percha, residues from petroleum-distillation, and numerous other ingredients enter into the composition of these preparations, either in addition to, or instead of, the ordinary constituents of paint. One of the most efficient waterproof paints on the market at the present time is stated to be the product known as 'Inertol.'

Anti-fouling, Anti-corrosive, or **Preservative paints, for Surfaces of Iron, Ship's Bottoms, &c.** Anti-fouling compositions are of two classes: (1) compositions which partly prevent the adhesion of testacea (barnacles), and partly kill these organisms by their active poisonous constituents; (2) compositions which gradually peel off in water and so cause the removal of the encrusting testacea. The property of peeling off is often possessed by poisonous paints of the first class. The best anti-fouling composition are poisonous enamels, which, in addition to possessing toxic properties, are quick drying, adhere with a smooth surface, and do not peel off. To prevent peeling a number of coats must be applied, each of which is allowed to dry uniformly. The harder the paint the longer it lasts. Hard paints are more suitable for Atlantic passages, and peeling enamels are better adapted for the water of the Indian seas. Copper salts, especially sulphates or oxides, form new combinations with the surrounding water and are gradually eaten away, *i.e.* peel off. Mercury, arsenic, copper, are metals commonly used in anti-fouling compositions. Japan lac has been tried with success in the Japanese navy.

The Preservation of Iron by paint. The presence of polymerised oil increases the durability of paint on exposure to air or water. The greatest permanence and protective power result when dark or red pigments are employed. White and light-coloured paints are inferior protectors. The proportions of pigment to oil are of importance, and in the case of deep Indian red maximum efficiency is attained with 60 p.c. pigment, whilst red-lead paint requires 80 p.c. pigment. The maximum protection coincides well with the ease of working and two coats protect better than one. The cheapest method and the one calculated to prolong the life of the metal is to paint iron or steel structures whilst the scale is still on the surface, after removing any loosely adhering flakes and rust. The coat of paint will last longer than if applied to pickled or sand-blasted surfaces (J. N. Friend, Carnegie Scholarship Memoirs, 1918, 10, 116). Many of these paints contain resinous constituents and resemble varnishes. Oxide of iron, pitch, shellac, rosin, tannin, silicates, fluorides, and fluorsilicates, &c., are often ingredients of these compositions. The protective power of the paint depends largely on the nature of the medium and the impermeability of the film to water. An emulsion of tar and clay is stated to be a highly protective coating for iron and timber. Effective rust-preventative preparations are known, which are brushed on bright steel parts of machinery, to prevent rust during transit, and can be easily removed with petroleum when required. Protective paints for Portland cement surfaces are described by H. A. Gardner (Amer. Soc. Testing Materials, 1914, 14).

Water and Washable paints. Ordinary distemper consists of whiting, China clay, &c., mixed with a hot solution of size and disinfectant, made up generally when required and tinted to any desired colour by stirring in pigments. The film dries by evaporation and is soluble in water. Many of the water paints on the market are washable when dry. The original medium of paints of this type was yolk of egg beaten up with water and mixed with pigment, forming the basis of tempera paintings. Albumen has now been replaced by glue or casein with an antiseptic. The miscibility with water is promoted by the presence of soap or by the partial saponification of a drying oil. On exposure the film dries by evaporation of water and by the oxidation of the drying oil with the evolution of volatile products, which gradually render the glue or the casein insoluble. It is probable that an aldehyde, *e.g.* formaldehyde, causes the insolubility of the protein material. The presence of drying oil with a refractive index approaching that of whiting or China clay requires substitution by pigments, which are commonly used in oil paints, *e.g.* zinc oxide lithopone, &c.

Enamels. These are brilliantly coloured paints, yielding smooth and lustrous coatings. Essentially they consist of oil varnishes, ground up with finely divided pigments and thinned with turpentine. In the system of painting by the application of enamels a priming coat, which dries without gloss and sets quickly to a rough surface, is followed by a coat consisting of pigments of maximum strength or opacity, ground in a medium containing a suitable quantity of driers. A high degree of fineness of pigment and the production of a 'flat' finish is necessary. A glossy enamel or a varnish does not hold or 'key' with glossy undercoats. The final or protective coating consists of a medium possessing special properties of weather resistance and flow, pigmented to such a degree that the natural or yellow colour of the varnish is overcome. In the best white enamels where zinc oxide is used a medium of thickened linseed oil is to be preferred, because a resin varnish would produce thickening by the interaction of acid and basic pigment, unless kauri or rosin esters are used. Generally 'stand' oil hardened with a small proportion of elastic gum varnish is used. The activity of the pigment must be carefully considered, as too rapid a rate of oxidation will produce a loss of gloss, owing to volume changes in the film. Another cause of loss of permanence of gloss is the oil solubility (bleeding) of certain lake pigments, notably madder. The relatively low opacity or tinctorial power of certain pigments is a source of difficulty, because the

degree of pigmentation must be maintained within limits. A good summary of the composition and properties of enamel paints is given by O. M. Meissl (J. Soc. Chem. Ind., 1914, 1099).

Such miscellaneous products as the so-called 'gold' paints and enamels (consisting of bronze-powders suspended in resinous varnishes, or in a solution of celluloid in amyl acetate and acetone); 'silver' paint (in which finely divided aluminium is the pigment); aniline-coloured aluminium paints; mica-scale paint; flexible paint; grease paints (tinted cosmetics); floor paints; roof paints; and the like, can receive but a bare mention here. Aluminium paint is now very extensively used.

For analysis of paints, *v.* ANALYSIS: also references below.

Literature.—J. Cameron, Oils and Varnishes, 1886; W. J. Russell and W. de W. Abney, Report on the Action of Light on Water Colours, 1888; Evidence and Report, Departmental Committee on the Various Lead Industries, 1894; R. Lemoine and C. du Manior, Manuel Pratique de la Fabrication des Couleurs, Paris, 1898; J. Bersch (trlr., A. C. Wright), The Manufacture of Mineral and Lake Pigments, 1901; A. H. Church, The Chemistry of Paints and Painting, 1901; E. J. Parry and J. H. Coste, The Chemistry of Pigments, 1902; G. H. Hurst, The Painter's Laboratory Guide, 1902; L. E. Andés (trlrs., A. Morris and H. Robson), Oil Colours and Printers' Inks, 1903; P. N. Hasluck, Painters' Oils, Colours and Varnishes, 1905; F. Diolé, Les Matières Premières employées dans La Peinture en Batiment, Paris, 1905; A. H. Sabin, The Industrial and Artistic Technology of Paint and Varnish, 1905; J. M. Thomson, The Chemistry of Artists' Colours in relation to their Composition and Permanency, Soc. Arts Jour. 54 (1905–6), 388–397; C. H. Hall, The Chemistry of Paints and Paint Vehicles, 1906; G. Zurr und R. Rübencamp, Handbuch der Farben-Fabrikation, Dresden, 1906; A. S. Jennings, Paint and Colour Mixing, 1906; A. P. Laurie, Oils, Varnishes, and Mediums used in the Painting of Pictures, Soc. Arts Jour. 55 (1906–7), 557–563; G. H. Hurst, Painters' Colours, Oils, and Varnishes, 5th ed., 1903; M. Toch, The Chemistry and Technology of Mixed Paints, 1907; J. G. Gentele (ed. A. Buntrock), Lehrbuch der Farbenfabrikation, Braunschweig, 1906–9; G. Petit (trlr., D. Grant), The Manufacture and Comparative Merits of White Lead and Zinc White Paints, 1907; J. C. Smith, Manufacture of Paint, 1919; C. D. Holley and E. F. Ladd, Analysis of Mixed Paints, Colour Pigments and Varnishes, New York, 1908; C. D. Holley, The Lead and Zinc Pigments, 1909; A. S. Jennison, Manufacture of Lake Pigments from Artificial Colours, 1920; A. Eibner, Malmaterialienkunde als Grundlage der Maltechnik, Berlin, 1909; J. N. Friend, An Introduction to the Chemistry of Paints, 1910; W. G. Scott, White Paints and Painting, Materials, Chicago, 1910; A. P. Laurie, Greek and Roman Methods of Painting, 1910; A. P. Laurie, Materials of the Painters' Craft, 1910; J. Marcusson, Laboratoriumsbuch für die Industrie der Öle und Fette, Halle, 1911; H. A. Gardner and J. A. Schaeffer, Analysis of Paints and Painting Materials, New York, 1911; Circular of the Bureau of Standards, No. 69 (Paint and Varnish), Washington, 1911; A. P. Laurie, Pigments and the Mediums of the Old Masters; L. E. Andés, Iron Corrosion, Anti-fouling and Anti-corrosive Paints, 1915; R. S. Morrell and A. de Wade, Rubber, Resins, Paints and Varnishes, 1921. E. G. C.

PALATINE ORANGE. This colouring matter is the ammonium salt of tetranitro-γ-diphenol. It is soluble in water, and dyes wool and silk orange in a bath acidified with acetic or sulphuric acid (Hummel, Dyeing of Textile Fabrics (1885), p. 401).

Tetranitro-γ-diphenol $C_{12}H_4(NO_2)_4(OH)_2$ is obtained by the action of fuming nitric acid on γ-diphenol or on benzidine, and melts at 220°; prolonged heating with concentrated nitric acid converts it into picric acid and oxalic acid (Schmidt and Schultz, Annalen, 207, 335).

PALAU. An alloy of gold and palladium used as a substitute for platinum, sp.gr. 17·22, m.p. 1370°. Crucibles made of 'palau' have all the good properties of those of platinum, except in pyrosulphate fusions.

PALISANDER WOOD. This name is now generally applied to one or more kinds of timbers that resemble rose-wood and are obtained in tropical South America and Mexico. The wood is lighter or darker violet brown or chocolate, and is marked by darker, often black, bands running with the grain. The actual origin of the timber is not known, but is attributed to the bignoniaceous *Jacaranda brasiliana* (Pers.) as well as to one or more species of the leguminous genera *Machœrium* and *Dalbergia*.

The name 'palisander wood' has apparently also been applied to an entirely different red dye-wood of unknown origin, obtained in Madagascar.

PALLADIUM. Sym. Pd. At.wt. 106·66. Occurs in all varieties of crude platinum and in many copper ores, especially in those which are nickeliferous and which are associated with pyrrhotine. It also occurs as an alloy with platinum or gold, especially in Brazil, and, in association with selenide of lead, in the Harz, in the form of hexagonal plates, although its normal crystalline form in other deposits is octahedral. Its principal source is the matte from the copper-nickel ores of Sudbury in Ontario. The palladium recovered by the refiners of bullion in the United States only is given as 2635 oz. in 1914, and 1541 oz. in 1915, but the figures are probably low. Other interesting information is to be found in the Report of the Royal Ontario Nickel Commission, Toronto, 1917.

Palladium has also been detected in a meteorite (Trottarelli, Gazz. chim. ital. 1890, 20, 611) and in the solar spectrum (Lockyer, Compt. rend. 1878, 86, 317).

Preparation.—Palladium is recovered from the solution left after precipitating platinum with ammonium chloride. It was discovered in these liquors by Wollaston (Phil. Trans. 1805, 95, 316). Palladium usually exists in solution as $PdCl_2$, though by oxidising with *aqua regia* or chlorine at a gentle heat in presence of potassium chloride a partial precipitation of the unstable K_2PdCl_6 may be obtained, which is converted back to the soluble chloropalladite by boiling with water, whereby chlorine is

evolved, or by reducing agents. Palladium salts warmed with ammonia are very readily converted into the soluble ammonia base from which, after cooling, hydrochloric acid precipitates the bright yellow crystalline palladosammine chloride $Pd(NH_3)_2Cl_2$. This, like all palladium salts, may be reduced to metal by gentle ignition in hydrogen and cooling in a neutral gas.

Palladium is separated also from the other platinum metals by adding mercuric cyanide to the neutral solution which precipitates the white dicyanide. This yields palladium metal on ignition. Copper, however, cannot be separated thus from palladium. To effect this the solution must be saturated with sulphur dioxide and KCNS added, which completely precipitates the copper as white cuprous thiocyanate, leaving the palladium in solution. α-nitroso-β-naphthol also precipitates palladium quantitatively, and may be used in the presence of copper and ferric iron (Wunder and Thüringer, Zeitsch. anal. Chem. 1913, 52, 737; also Schmidt, Zeitsch. anorg. Chem. 1913, 80, 335). Palladium may also be precipitated from a slightly acid solution by adding dimethyl glyoxime, which gives a bulky orange precipitate of $C_8H_{14}N_4O_4Pd$, soluble in dilute alkali but insoluble in boiling water, with which it may be washed. Nickel is precipitated by the same reagent from an ammoniacal solution, and consequently dimethyl glyoxime may be used for a quantitative separation of palladium and nickel (Wunder and Thüringer, Ann. Chim. anal. 1912, 17, 201, 328; also Zeitsch. anal. Chem. 1913, 52, 660). Palladium is completely reduced from dilute chloride solution by hydrazine sulphate with evolution of nitrogen (Jennasch and Bettges, Ber. 1904, 37, 2210; also Gutbier and Falco, Zeitsch. anal. Chem. 1910, 49, 287), also by boiling ferrous sulphate, hydrogen and acetylene.

Literature.—Bunsen, Phil. Mag. 1868, [iv.] 36, 253; Philipp, Dingl. Poly. J. 1876, 220, 95; Guyard, Compt. rend. 1863, 56, 1177; Leidié, *ibid.* 1900, 131, 888; Orloff, Chem. Zeit. 1906, 30, 714.

Palladium is a silver-white metal of the same hardness as platinum (38, Brinell). It has a sp.gr. of 11·97 (Violle) and melts at 1546° (Waidner and Burgess, J. Soc. Chem. Ind. 1907, 1140), 1550° (Dana and Foote, Trans. Farad. Soc. 1920, 15, 186). When heated to low redness in air, it becomes bluish, but it regains its white appearance at higher temperatures. At the melting-point of iridium it boils and volatilises as a green vapour with partial oxidation.

It unites with fluorine and chlorine at a dull red heat, and superficially with iodine when treated with alcoholic iodine solution. Palladium is readily attacked by *aqua regia* in the cold and also by boiling sulphuric acid. It dissolves completely in hot sulphuric and nitric acids (1 : 1 : 2 *aqua*) and in selenic acid (Hradecky, Monatsh. 1915, 36, 289). It unites with sulphur and selenium, less readily with phosphorus and arsenic, and with silicon at a white heat. It forms alloys with many metals; and unlike platinum will alloy with silver in all proportions. The nickel alloys are magnetic up to 87 p.c. palladium, but rapidly less so above 40 p.c. palladium (Heinrich, Zeitsch. anorg. Chem. 1913, 83, 322).

Palladium melted with gold forms a number of alloys which have recently become important as substitutes for platinum. 'Rhotanium' contains 60–90 p.c. of gold, and for certain purposes a small proportion of rhodium is essential. Its sp.gr. is between 16 and 18·5 and m.p. about 1450°. The volatilisation loss at 1050°–1400° is low. It can be welded at a white heat without flux, and is useful in dental work, for jewellery, and for electrical contacts, though not for magnetos or as an anode in electrolysis (Fahrenwald, J. Ind. Eng. Chem. 1917, 9, 590). 'Palau' is another palladium gold alloy with sp.gr. 17·22 and m.p. 1370°. It will withstand the action of $HCl, HNO_3, HF, H_2SO_4, NaOH$ in solution and fused Na_2CO_3, comparing favourably with platinum (Met. & Chem. Eng. 1917, 16, 533). 'White 18 carat' is a jeweller's hard alloy to replace platinum for diamond mounting. It contains 18 parts of fine gold in 24 and the balance mainly palladium which imparts its whiteness to the alloy.

Palladium has been employed for the graduated circles, &c., of philosophical instruments, and, to a small extent, in watch-making, and has been used for the electro-plating of parabolic mirrors on account of its silvery appearance and absence of change on exposure to impure air. It can also be used for soldering platinum, but the bulk of the output is employed in the manufacture of dental alloys, and since 1916 in the manufacture of jewellery, chiefly in place of platinum for diamond mounting.

Palladium, in the form of palladised asbestos, is said to give excellent results when used as a contact substance in combustion analyses. It may be prepared for this purpose by precipitating a solution of pure palladium chloride in the presence of asbestos, by means of alkaline sodium formate (Jacobsen and Landesen, Ber. 1907, 40, 3217; Dennstadt, *ibid.* 3677).

Palladium, in the form either of sponge or black, has catalytic properties in a greater degree than platinum. According to Willstätter and Waldschmidt-Leitz its use for catalytic hydrogenation depends on the presence of oxygen in the catalyst.

Literature on the catalytic properties of palladium and of colloidal palladium: Coquillon, Compt. rend. 1878, 87, 795; Phillips, Zeitsch. anorg. Chem. 1894, 6, 213; Lunge and Akunoff, *ibid.* 1900, 24, 191; Kraut, Ber. 1887, 20, 1113; Jahn, *ibid.* 1889, 22, 989; Zelinsky, *ibid.* 1898, 31, 3203; Bredig and Fortner, *ibid.* 1904, 3, 798; Paal and Roth, *ibid.* 1908, 41, 2273, 2282; *ibid.* 1909, 42, 1541, 1553; *ibid.* 1910, 43, 2684, 2692; Paal and Gerum, *ibid.* 1909, 2273; Paal and Büttner, *ibid.* 1915, 48, 220; Willstatter and Waldschmidt-Leitz, *ibid*, 1921, 54 [B], 113.

Palladium absorbs various gases in quantities varying with its physical state (Cailletet and Collardeau, Compt. rend. 1894, 119, 830; Mond, Ramsay and Shields, Proc. Roy. Soc. 1897, 62, 290; Harbeck and Lunge, Zeitsch. anorg. Chem. 1898, 16, 50). For the adsorption of acetylene by colloidal palladium, *see* Paal and Hohenegger, Ber. 1910, 43, 2684, 2692; also 1913, 46, 128; 1915, 48, 275.

At ordinary temperatures, a palladium wire will absorb between 300 and 400 times its bulk of hydrogen and, when heated to redness

in hydrogen, it absorbs nearly 1000 volumes and increases in bulk by nearly 10 p.c. This 'alloy' of hydrogen and palladium is permanent in air and *in vacuô* at ordinary temperatures, but yields up the whole of its hydrogen when heated *in vacuô* (Mond, Ramsay and Shields, Chem. News, 1897, 76, 317; Dewar, *ibid.* 274; Fischer, J. Soc. Chem. Ind. 1906, 993); also Gutbier, Gebhardt and Ottenstern, Ber. 1913, 46, 1453; Holt, Proc. Roy. Soc. 1914 [A], 90, 226; 1915 [A], 91, 148; Sieverts, Zeitsch. angew. Chem. 1914, 27, 337). Alloys of palladium also absorb hydrogen, and the ones with silver absorb more hydrogen than pure palladium. 40 p.c. silver-palladium at 138° will absorb four times as much hydrogen as the pure metal (Sieverts, Jurisch and Metz, Zeitsch. anorg. Chem. 1915, 92, 329). For observations on the occlusion of hydrogen by the palladium gold alloys, *see* Berry (Chem. Soc. Trans. 1911, 99, 463). For the inhibiting effect of hydrogen sulphide on the occlusion of hydrogen by palladium, *see* Maxted (Chem. Soc. Trans. 1919, 115, 1050; 1920, 117, 1280). On the sorption of hydrogen by amorphous palladium, *see* Firth (Chem. Soc. Trans. 1921, 1120).

'Palladium hydrogen' is a valuable reducing agent (Sabatier and Senderens, Compt. rend. 1892, 114, 1430; Engel, Compt. rend. 1899, 129, 518; Keiser, Ber. 1887, 20, 2323).

In presence of water and of oxygen, palladium hydrogen seems to behave as an oxidising agent, this being probably due to the formation of hydrogen peroxide, which, in the presence of palladium, behaves as the oxidiser (Traube, Ber. 1889, 22, 1496; Hoppe-Seyler, *ibid.* 2215).

The salts of palladium have so far been but little applied to technical use, but some of them, like potassium chloropalladite, are employed for toning in photography (J. Soc. Chem. Ind. 1911, 1410).

Palladium Compounds.

Oxides. **Palladium monoxide** PdO may be prepared as an amber-coloured mass, yielding a black powder, by heating a mixture of a palladium salt with potassium carbonate; or as a bluish-green mass by heating the spongy metal in a current of oxygen at 700°–840°. It acts as a powerful oxidising agent to organic substances, and is reduced to metal by hydrogen or hydrogen peroxide. When freshly precipitated in the cold from a palladous salt with sodium carbonate, the *hydroxide* is dark brown, and is readily soluble in alkalis. If dried or precipitated from a boiling solution it becomes insoluble. The *palladous* salts which correspond to this oxide are of green, red, or brown colour, and have an astringent taste. A solution of palladous hydroxide organosol in paraffin oil has been introduced as a therapeutic agent under the name of 'Leptynol.'

Palladium dioxide PdO_2 may be obtained in an impure hydrated form, soluble in acid, by the interaction of caustic soda and a palladichloride, or in a purer form, by the anodic oxidation of the nitrate (Wöhler and König, Zeitsch. anorg. Chem. 1905, 46, 323; *ibid.* 1906, 48, 203). It is a vigorous oxidising agent.

Palladium sesquioxide Pd_2O_3 is best prepared by the electrolytic oxidation of a concentrated solution of palladous nitrate at 8° with a current density of 0·5 cm. amp./cm²; but if the electrolysis is prolonged, the dioxide is formed (Wöhler and Martin, *ibid.* 1908, 57, 398). It forms a dark brown unstable powder; gives unstable solutions in hydrochloric acid, and when suspended in ether and mixed with alkali chlorides, on addition of hydrochloric acid, the double chlorides $PdCl_3,2MCl$ are formed, which in contact with water yield the salts M_2PdCl_4.

Halogen compounds. **Palladous chloride** $PdCl_2$ may be prepared by the action of air or of chlorine and hydrochloric acid on the metal, or by heating palladous sulphide in dry chlorine (Matignon, Compt. rend. 1903, 137, 1051).

It crystallises with 2 mols. of water with a reddish-brown colour; loses water on heating and becomes dark brown, and at a red heat forms the *monochloride* PdCl, a red-brown crystalline deliquescent mass. Palladous chloride combines with carbon monoxide, yielding the crystalline compounds $PdCl_2{\cdot}CO$, m.p. 197°; $PdCl_2{\cdot}2CO$, m.p. 142°; $2PdCl_2{\cdot}3CO$, m.p. 132° (Fink, Compt. rend. 1898, 126, 646).

Palladous chloride forms double chlorides with other metals known as *chloropalladites* of the type M_2PdCl_4 (Gutbier and Krell, Ber. 1905, 38, 2385), of which the potassium salt is used in photography for toning (J. Soc. Chem. Ind. 1901, 154; Kessler, *ibid.* 849).

Many organic basic derivatives of these salts are known (Hardin, J. Amer. Chem. Soc. 1899, 21, 943; Rosenheim and Maass, Zeitsch. anorg. Chem. 1898, 18, 331; Gutbier, Ber. 1905, 38, 2105; Gutbier and Krell, *ibid.* 3869; *ibid.* 1906, 39, 616, 1292; Gutbier and Woernle, *ibid.* 2716).

Palladic chloride is not known in the free state, but only as double salts of the type M_2PdCl_6, and in combination with tertiary cyclic organic bases, and with tertiary bases, as intensely coloured products (Mohlan, Ber. 1906, 39, 861; Gutbier and Woernle, *ibid.* 4134). The ammonium and potassium salts form bright red octahedra, but the sodium salt is extremely soluble and has not been obtained in the crystalline form.

The **trichloride** $PdCl_3$ is obtained as above, and in the form of double salts M_2PdCl_5 (Wöhler and Martin, *l.c.*). Bromides and iodides of palladium are also known (Gutbier and Krell, *l.c.*; Smith and Wallace, Zeitsch. anorg. Chem. 6, 380).

Ammonia salts. Ammonia acts on palladous salts forming *palladosammine* and *palladodiammine* compounds, analogous to the corresponding platinum compounds (Müller, Annalen, 1853, 86, 341). Palladium derivatives of hydroxylamine (Zeisel and Nowack, Annalen, 1907, 351, 439) and of hydrazine chloride (Burdakoff, J. Russ. Phys. Chem. Soc. 1909, 41, 757) have been prepared.

When a 33 p.c. solution of a primary alkyl amine is added slowly to an excess of palladous chloride or bromide solution, rose-red needles of a salt $Pd(NH_3)_4X_2PdX_2$ are thrown down. These salts are readily converted into palladosammine derivatives of formula PdR_2X_2 (R=mol. of amine, X=halogen) by (*a*) heating to 200°, (*b*) by evaporating their aqueous solution, (*c*) by solution in warm alkali and precipitation with the desired halogen hydride.

The palladosammine chlorides are of a pale-yellow colour, the bromides dark-yellow, and the iodides brownish-yellow. They all yield colourless solutions in concentrated ammonium hydroxide (Gutbier and Krell, Ber. 1906, 39, 1292; Zeitsch. anorg. Chem. 1905, 47, 23). Certain diamines also yield rose- or flesh-coloured salts with palladous halides of the composition PdD_2X_2,PdX_2 (X=halogen, D=diamine) (Gutbier and Woernle, Ber. *l.c.*; *see* also Rosenheim and Maass, *l.c.*).

Palladous nitrate $Pd(NO_3)_2$ is formed by dissolving the metal or the oxide in nitric acid. It forms brownish-yellow deliquescent prisms, which on addition of water are converted into a brown powder of composition $Pd(NO_3)_2$,$3Pd(OH)_2$.

Potassium palladonitrite $Pd(NO_2)_4K_2$ is a pale-yellow crystalline powder formed by adding potassium nitrite to a hot solution of potassium palladochloride, and according to Pozzi-Escot and Couquet (Compt. rend. 1900, 130, 1073), this may serve as a micro-chemical test for palladium.

Palladous cyanide is a pale-yellow salt obtained by the action of mercuric cyanide on a palladous salt.

Palladous thiocyanates are described by Belucci (Atti R. Accad. Lincei, 1904, v. 13, ii. 386).

Palladous sulphate $PdSO_4$,H_2O, formed by the solution of the hydroxide in sulphuric acid, forms olive-green crystals which are decomposed by water forming a basic salt $Pd(SO_4)$,$7Pd(OH)_2$.

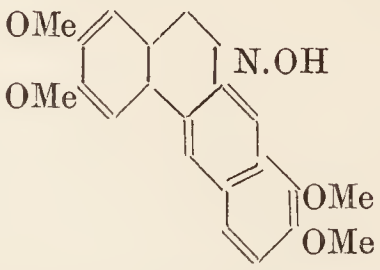
The *sulphides* Pd_2S, PdS, and PdS_2; *selenides* (Roessler, Zeitsch. anorg. Chem. 1895, 9, 31; *see* Petrenko-Kritchenko, *ibid.* 1893, 4, 247), and also *thiosulphates* are known (*see*, too, Hofman and Höchtlen, Ber. 1904, 37, 245).

Palladium silicides are formed when the elements are heated together to 500°–600° (Lebeau and Jolibois, Compt. rend. 1908, 146, 1028).

A number of complex nitrites, sulphites, phosphates, and oxalates have been prepared (Loiseleur, Compt. rend. 1900, 131, 262; Vézes, Bull. Soc. chim. 1899, [iii.] 21, 172; Rosenheim and Itzig, Zeitsch. anorg. Chem. 1900, 23, 28).

For certain other organic compounds of palladium, *see* Hofmann and Rabe, *ibid.* 1897, 14, 293; Kurnakoff and Swosdareff, *ibid.* 1889, 22, 384. A. J. W.

PALMATINE. A substance isolated from calumba root by Feist and found to have the formula:



(Feist and Standstede, Arch. Pharm. 1918, 256, 1). This formula is analogous to that of berberine, and this substance has been converted into palmatine by Späth and Lang (Ber. 1921, 54, [B] 3064) by replacing the hydroxymethylene group of berberine and replacing it by two methoxyl groups, *v.* Calumba.

PALMATISINE *v.* Aconitine.

PALMERITE *v.* Minervite.

PALMIACOL (*Cetiacol*). Syn. for pyrocatechol methyl cetyl ether.

PALMITIC ACID $CH_3[CH_2]_{14}COOH$ is a constituent of the greater number of animal and vegetable fats, in which it occurs as the glyceride *tripalmitin* $C_3H_5(C_{16}H_{31}O_2)_3$. It is obtained from palm-oil (whence its name) by saponification; also by treating oleic acid with caustic alkali. It also occurs in Chinese tallow (from *Sapium sebiferum* [Roxb.]), in Japanese wax (from *Rhus succedanea* [Linn.]), in butter, spermaceti, human fat, lard, &c. (Frémy, Annalen, 36, 44; Maskelyne, J. 1855, 519; Brodie, Annalen, 71, 159; Krafft, Ber. 1888, 2265; Varrentrapp, Annalen, 35, 210). Crystallises from alcohol in needles; m.p. 62·6°, and distils, with slight decomposition, between 339° and 356°, b.p. 268·5° (100 mm.); sp.gr. 0·8527 at 62°/4°. It is much more soluble than stearic acid in alcohol, and on this difference is based the method of estimating stearic acid in fats (*see* Oils, Fixed, and Fats).

Cetyl palmitate $C_{16}H_{31}O_2C_{16}H_{33}$ is the chief constituent of spermaceti (Heintz, Annalen, 80, 297). Crystallises from ether in thin plates; m.p. 53·5°.

Ceryl palmitate $C_{16}H_{31}O_2C_{27}H_{55}$ is the main constituent of opium wax (Hesse, Ber. 1870, 639); m.p. 79°. *Myricyl palmitate*

$$C_{16}H_{31}O_2C_{30}H_{61}$$

is found in beeswax (Brodie, Annalen, 71, 159); m.p. 72°.

By heating palmitic acid with glycerol, the mono-, di-, and tri-palmitins are prepared. *Tripalmitin* melts at 62° (Chittenden and Smith, Amer. Chem. J. 6, 230; Stenhouse, Annalen, 36, 54).

For estimation and other details, *v.* Oils, Fixed, and Fats.

PALMITIN *v.* Oil, Fixed, and Fats.

PALM KERNEL OIL. Palm kernel oil is obtained from the kernels of the palm tree fruit. The kernels are collected by the natives after the palm oil has been recovered from the fleshy part of the fruit; the shells are removed by cracking each nut separately with a stone or hammer. This work is chiefly done by women and children. Owing to the laboriousness of this process, and also to the fact that no more than about 15 pounds of kernels are obtained by one worker in a day, and that the kernels have to be carried to the market, enormous quantities of palm nuts are wasted. Although of recent years nut-cracking machines have been sent to the west coast of Africa, they have hitherto not been able entirely to supplant manual labour. The kernels are collected at the coast stations and shipped to Europe. The chief receiving ports are Hamburg, Liverpool, and Marseilles.

In Europe the kernels are screened to free them from shells, stones, nails, hammerheads, then passed over magnetic separators, and many ground between rollers to a paste. The pulpy mass is either expressed in hydraulic presses or extracted with solvents. In the first process the meal must be pressed twice, on account of the large proportion of fat the kernels contain.

On a commercial scale, the first expression of palm kernel meal is carried out at a temperature of 45°–50°, the second at 55°–60°. Thus 43–45 p.c. of palm kernel oil is recovered.

The press cake contains 6–8 p.c. of oil; its proportion of nitrogen is small (about 2·5 p.c.),

hence its value as cattle food is somewhat low. For the same reason the extracted meal has a low manurial value.

The colour of palm kernel oil is white to pale yellow. In the fresh state the oil is neutral and has a pleasant smell and an agreeable nutty taste. Commercial samples contain, however, notable amounts of free fatty acids.

For physical and chemical characteristics, *v.* tables under OILS, FIXED, AND FATS.

The chief constituent of palm kernel oil is lauric acid. In addition, there are present smaller quantities of caprylic, capric, caproic, myristic, palmitic, stearic, and oleic acids.

Palm kernel oil is largely used for soap-making. The freshest oil is employed in the manufacture of margarine (like 'coconut oil') and of 'chocolate fat.' In this latter manufacture a hard fat ('palm nut stearine') is obtained; the liquid 'palm nut oleine,' being a by-product, is used in soap-making.

Fats of similar character are produced by other species of palms. The characteristics of some of the more important of these of Brazilian origin have been described by Bolton and Hewer (Analyst, 1917, 42, 35; 1922, 47, 282, and Bray and Islip, *ibid.* 1921, 46, 325. For a method of estimating coconut and palm kernel oils in mixtures which may contain both fats, see Stokoe, J. Soc. Chem. Ind. 1921, 40, 57 T. J. L.

PALM OIL. Palm oil is obtained from the fleshy part of the ripe fruit of the palm tree *Elæis guineensis* (Jacq.), which forms vast forests along the west coast of Africa, extending between Gambia and St. Paul de Loanda. The west coast of Africa is practically the only supplier of palm oil. *Elæis guineensis* forms a very large number of sub-species for the description of which the reader may be referred to 'Le Palmier a l'Huille' by Jean Adam (Challamel, Paris).

The favourite habitat of the palm tree is the open country or bushland; it grows frequently where the natives have cleared the virgin forest. The tree is characteristic of the coast line and the lower reaches of the rivers. It will grow in all soils, but does not bear well at a higher elevation than 3000 feet. Under favourable conditions the tree forms a trunk when five years old, and then begins to bear fruit. The yield afterwards increases and the tree gives its full harvest in its 12th year. This rate of yield is continued throughout the life of the palm tree, which lasts 50–60 years.

Owing to climatic conditions, the process of extraction has been hitherto practised exclusively by the natives, and is an exceedingly crude one. When the fruits ripen, the men climb up the trees and cut off the bunches with 'matchets.' Owing to the height from which the bunches fall, a large quantity of the fruit is bruised, which naturally leads to rapid fermentation and to hydrolysis of the oil. The women and children pick the fruit from the bunches and throw it into a hole dug in the ground and lined with leaves. The flesh of the fruit is at this time hard, and before the kernels can be separated, the flesh must be softened. This is done by sprinkling water on the fruit, covering it over with more leaves, weighted by stones and wood, and leaving for about two weeks. During this period fermentation sets in, which causes the fleshy part of the fruit to become soft, so that the kernel—palm nut—can be removed more readily. This is done by men, who place the fermented fruits in a mortar, roughly made by lining a hole made in the ground with large flat stones. The fruit is then beaten with long wooden pestles, or the pulp is pressed by hand. The beaten pulp, together with the nuts, is taken out by women and children and placed over another hole, the sides of which have been cemented by plastering with a mixture of palm oil and wood ashes. The pulpy mass is then allowed to rest for a week. During this time, the oil drains into the cemented hole, from which it is ladled out into large calabashes of a size to make up one load.

The oil so prepared represents a superior kind of product. Women and children then pick out the nuts from the pulp, mix the pulp with water and place it in large iron cauldrons, where the whole mass is well boiled and stirred until the oil rises to the top. The oil is skimmed off, and, in some regions, mixed with the first extracted oil or put into separate vessels for the market. Finally, the residue is placed in a bag and squeezed over a hole so as to force out the liquid, from which more oil rises to the top. This oil contains a large quantity of water, and is again boiled out, skimmed off, and placed in calabashes.

The oil is carried—mostly by women—to the nearest coast or river station, where traders collect it in large barrels, and take it down to the coast station. There the oil frequently undergoes a rough purification by being boiled up with water, whereupon it is poured through sieves into barrels ready for shipment. Efforts have been made to introduce European methods of manufacture in the coast stations as well as in the bush in the French, English, and Congo territories at the west coast of Africa.

Palm oil has a somewhat sweetish taste; in its perfectly fresh state it is used as a culinary fat in the villages of the west coast of Africa. Its odour is pleasant and resembles that of violets; this odour is not destroyed by bleaching with air at elevated temperatures, and persists even after the oil has been made into soap. In consequence of the very crude mode of producing palm oil, causing it to remain for a considerable time in contact with fermentable vegetable tissue, hydrolysis rapidly sets in, so that the oil on reaching the coast contains already a notable amount of free fatty acids. Palm oil when shipped from the coast has at least 10–12 p.c. of free fatty acids. The process of hydrolysis, once begun, continues in the barrels during the voyage, and in consequence, commercial palm oils, on arriving at their destination, contain frequently from 20–50 p.c., and even more, of free fatty acids. In such palm oils, free glycerol is found. In old samples the hydrolysis may even reach completion, so that such palm oil practically consists of free fatty acids (Lewkowitsch). The progress of hydrolysis may be observed even in oils kept in glass bottles.

The value of a palm oil in the market depends on the care with which it has been prepared, as also on the particular locality from which it is derived. The 'soft' oils are those containing a small quantity of free fatty acids,

whereas the 'hard' oils contain a large proportion. The best 'soft' oils come from Lagos and Dahomey. Next in quality are the river oils ('medium' oils); whilst the lowest quality, the hardest oil, is represented by Congo oil.

The colouring matter of palm oil is not affected in the process of saponification by means of caustic alkalis or lime; in the acid saponification process it is destroyed. It is also slowly destroyed by exposure to air, more rapidly on heating or by bleaching with chemicals. The two latter processes are adopted in practice for preparing bleached palm oil.

The bleaching process most in vogue, and that giving the best results, is the dichromate process. The oil is freed from its gross impurities, and treated according to its quality with 1–3 p.c. of potassium dichromate and the requisite amount of hydrochloric acid. The dark 'chrome' liquor is then carefully run off, and the oil is washed with water, at first with the assistance of a little mineral acid, until it is quite free from chromium compounds and mineral acid.

Not all palm oils can be bleached successfully. Lagos and Old Calabar oils yield good results, but dirty-coloured red oils, such as Congo oils, have hitherto withstood all attempts to bleach them.

The chief constituents of palm oil are palmitin and olein. The proportion of stearin hardly exceeds 1 p.c. For the chemical and physical characteristics of palm oil, *v.* tables under Oils, Fixed, and Fats.

Palm oil is chiefly used in the soap and candle industries. In the latter industry it is valued *cæteris paribus* by its 'titer.' It is also employed in America as a colouring matter for margarine. Being a non-drying oil, it is also employed in the tin-plate industry, to preserve the surface of the heated iron sheet from oxidation until the moment of dipping into the bath of melted tin.

For the purposes of the tin industry, 'palm oil greases' are sold, consisting of palm oil adulterated with cotton-seed oil and mineral oil of the sp.gr. 0·905. J. L.

PALM RESIN or **CEROXYLIN** *v.* Resins.

PALM SUGAR or **DATE-TREE SUGAR.** The liquid extract of certain palms is more or less rich in saccharine substances which are easily separated from such liquids. A method of obtaining sugar from this extract has existed in India from time immemorial, and was found to prevail among the aborigines of America on the discovery of that continent.

The palms which supply sugar are *Borassus flabellifer* (Linn.), *Phœnix sylvestris* (Roxb.), *Caryota urens* (Linn.), *Arenga saccharifera* (Labill.), &c.

Palm sugar is hygroscopic, and appears to be purgative if freely used. To divest it of this property it requires to be refined. The juice is sometimes obtained by cutting off the lower leaves of the crown about the end of October, and stripping the trunk of such as grow upon it to the place where incision is to be made. A bamboo cane is placed at the orifice each evening, by means of which the sap is conducted into vessels which are removed early next morning. In the case of *Phœnix sylvestris*, the tapping is done by making an incision in the wood at the base of the lowest green leaves, and subsequently removing slices of wood until the flow ceases. The cut axis of the inflorescence of *Caryota urens*, and the cut flower axes and cut sheathing spathes of *Borassus flabellifer* yield the sugary juice. The process of extracting the sugar from the sap must be proceeded with without delay, as fermentation sets in rapidly, when it is impossible to procure by boiling the syrup or *goor*, *i.e.* the mixture of molasses and crystallised sugar from which the sugar is extracted. The amount of sugar produced is about 40 p.c. of the syrup.

PALM TREE WAX *v.* Waxes.

PALYGORSKITE *v.* Pelolite.

PANCLASTITE *v.* Explosives.

PANDERMITE. A natural calcium borate employed in the manufacture of enamels instead of borax, *v.* Colemanite.

PANICULATINE $C_{29}H_{35}O_7N$, an alkaloid found in the tubers of *Aconitum paniculatum*, Lam. Crystallises from methyl alcohol in small rhombic prisms, m.p. 263° (Brunner, Schweiz. Apoth. Zeit. 1922, 60, 357). Is not identical with aconitine.

PANTOPON (*Omnopon*). Trade name for a mixture of the soluble hydrochlorides of opium alkaloids.

PAPAIN or **PAPAYOTIN.** A vegetable digestive ferment obtained from the unripe fruit of *Carica Papaya* (Linn.), or papaw tree, and used as an alternate to pepsin, from which it differs by being active in neutral and alkaline conditions (*v.* E. J. Easter, Pharm. J. 1885, 45). The half-ripe fruit when scratched exudes a large quantity of a milky juice, which when dry forms a powder somewhat resembling gum arabic. The name 'papain' is usually restricted to the pure ferment associated with a proteid substance, and is obtained by precipitation with alcohol and separation of albuminous matter by basic lead acetate. The fruit of the papaw tree has long been used in the West Indies to render beef tender. The unripe fruit is split open and rubbed over the surface of the meat previous to cooking. Its action probably depends upon the fact that papain has a digestive action, not only upon muscular fibre, but also upon connective tissue. It digests fibrin and albumin in neutral and slightly alkaline solutions. When injected into the circulation in large doses it paralyses the heart. In smaller quantities it appears to favour the multiplication of micrococci in the blood (T. Lauder Brunton, Pharmacology, &c., 927).

For methods of determing its digestive value, *see* Graber (Analyst, 1912, 57), Rippetoe (J. Ind. Eng. Chem. 1912, 4, 517), Pratt (Analyst, 1915, 405).

PAPAVERALDINE, PAPAVERAMINE, PAPAVERINE *v.* Opium.

PAPER. The art of paper-making consists in uniting or 'felting' together any fibrous vegetable matter, so as to form a continuous sheet. Owing to the abolition of the paper duties, in 1827, and the consequent rapid growth of cheap literature, the old dictionary definition of paper as 'a substance made of linen or cotton rags' no longer holds good. As a matter of fact, these substances constitute but a small fraction of the raw materials of the paper-maker.

Any vegetable substance possessing a sufficiently fibrous structure can be utilised. Occasionally both animal and mineral fibrous

substances—such as wool, silk, or asbetos—are employed, either alone or as admixtures.

In order to give some idea of the variety of materials from which paper can be or has been manufactured, we may cite a book that was published at Regensburg, Germany, by Jacob Schaeffer in 1765, the paper of which was made from about sixty different sources, amongst which the following are curious and interesting: sawdust, hop-vines, hornets' nests, peat, straw, cabbage-stumps, moss, various woods, thistle-stalks. In the majority of cases the paper is of very inferior quality, the pulp being coarse and unbleached. A similar book is that containing the poems of the Marquis de Villette, published in 1786. Another, of historical interest, is one the paper of which was made entirely from straw. It was published in England in 1800.

Notwithstanding the variety of materials available, rags of various kinds continued to form the chief raw material of the paper-maker until the year 1860, when Mr. Thomas Routledge introduced esparto grass (*v.* ESPARTO). This material, which possesses many advantages, is very extensively used in this country. Of late years, however, owing to the enormous increase in the demand for paper, it has been largely supplemented by straw, and more especially by wood.

The chemical characteristics of the paper-makers' raw materials have already been discussed in the article CELLULOSE. These materials consist, with the exception of cotton and linen rags, of one or other, or a mixture, of the various compound celluloses; and the treatment they undergo consists essentially in isolating the cellulose by chemical means. This treatment is accompanied by separation, more or less complete, into individual cells, which vary in length from about 1·5 mm. in the case of esparto to 30 mm. in the case of flax. This chemical splitting up into cells is supplemented by a mechanical operation known as 'beating,' whereby the material is still further reduced (*v. infra*).

The various processes that the different forms of cellulose undergo before being made into paper may be divided into four main branches—(1) cleaning, (2) boiling, (3) bleaching, (4) beating, or reducing to pulp. In addition to these, there are the processes of sizing, colouring, &c., which will be included in No. 4.

1. Cleaning. This is a purely mechanical process, and consists in removing from the raw material adventitious matter, such as sand, dirt, &c. Part of this work is done by hand-labour, especially in the case of rags, but the modern tendency is to replace hand-labour as much as possible by machinery.

It is customary now for the various classes of rags to have a preliminary grading before reaching the paper mill. In this way each mill can obtain such supplies as would be suitable for its particular requirements, and to a larger extent obviates a re-selling of the raw materials which are useless for its purpose. It only requires therefore a further separation and subdivision of such types of raw material to produce special characteristics in the finished paper. Usually this work is done by girls, and it is during this final grading that hand cutting as well as the removal of pieces of metal, rubber, buttons and other impurities are effected. In mills producing high-grade papers, and where cutting by machinery is resorted to, the first operation still holds, for it is absolutely essential to open up the material by a preliminary cutting process. It is usually carried out on a series of large tables, each being fitted with a cutting knife and a metal lattice work top, through which a great deal of dust and many of the smaller pieces of metallic impurities can pass through into a shaft, at the end of which is placed a fan drawing air through. Such a method serves two purposes, in that the atmosphere is kept quite fresh and free from dust for the operatives, and also the dust is drawn into a common chamber from all the sorting tables. The rags which are thus sorted out and graded are usually put into sacks, and when sufficient material of each kind is obtained, put through a 'duster' for the final dusting operation. This consists of a hollow truncated cone-shaped cylinder placed horizontally, the sides of which consist of rigid iron bars fitted together with stays and to a central shaft, the whole being covered over with coarse wire netting. Inside the cylinder and fixed to the central shaft are projecting teeth about 6 inches long, which retain the material for a moment and then drop it to the side as the cylinder revolves, the rags meanwhile being gradually brought forward to the end of the machine, and either dropping direct into boxes or carried on to an endless band direct to the boilers.

2. Boiling. The boiling processes vary considerably with the kind of material. We will discuss them in the order of their simplicity.

(*a*) *Rag boiling.* Rags, being for the most part refuse from textiles made from pure or nearly pure cellulose, require a comparatively light treatment. It may be conducted either in spherical or cylindrical boilers, or in the 'vomiting' boilers, described under Esparto. In the case of spherical boilers the heating is caused by 'live' steam: cylindrical boilers are usually jacketed. It is preferable to cause the boilers to revolve. They are furnished with inlet and outlet steam-pipes, pipes for running in liquor and water, man-holes for filling and emptying, and safety valves, pressure gauges, &c. The alkali employed may be either caustic soda, caustic lime, sodium carbonate, or a mixture of the latter. The proportion of alkali depends mainly on the state of the rags and the nature of the substances to be removed, and also to some extent on the pressure of steam employed and the duration of the operation. As a general rule applicable to rags and all other fibres, it may be stated that the higher the pressure and the longer the time occupied, the less alkali (within, of course, certain limits) is necessary. The amount of alkali varies from 1 p.c. of 70 p.c. caustic soda in the case of the higher qualities of rags to 5 p.c. in the case of lower qualities.

The pressure also varies considerably—say, from 5 to 60 lbs. per square inch. In the opinion of some the lower pressures are to be preferred, as at the high temperature associated with higher pressure there is a tendency to fix a certain amount of dirt and colouring matter in the rags, thereby defeating to some extent the object of the boiling. After boiling, the rags may be

washed in the boiler or in a separate washing engine which will be subsequently described.

(*b*) *Esparto boiling.* Esparto, being a compound cellulose, requires a more drastic treatment than rags. The first process that esparto undergoes is that of 'picking.' This operation, which is done by hand, consists in removing root-ends, weeds, &c. It has latterly been largely dispensed with, and a more complete mechanical treatment substituted. For this purpose the grass is passed through a willow and duster similar in principle to that described under the head of Rags.

After passing through the machine the grass is in some cases carried along a travelling belt, and is discharged direct into the boiler. These are almost invariably stationary, as a revolving boiler is apt to cause the grass to form into dense masses, which resist the action of the soda used in boiling. An esparto boiler is shown in Fig. 1. It is furnished with a perforated

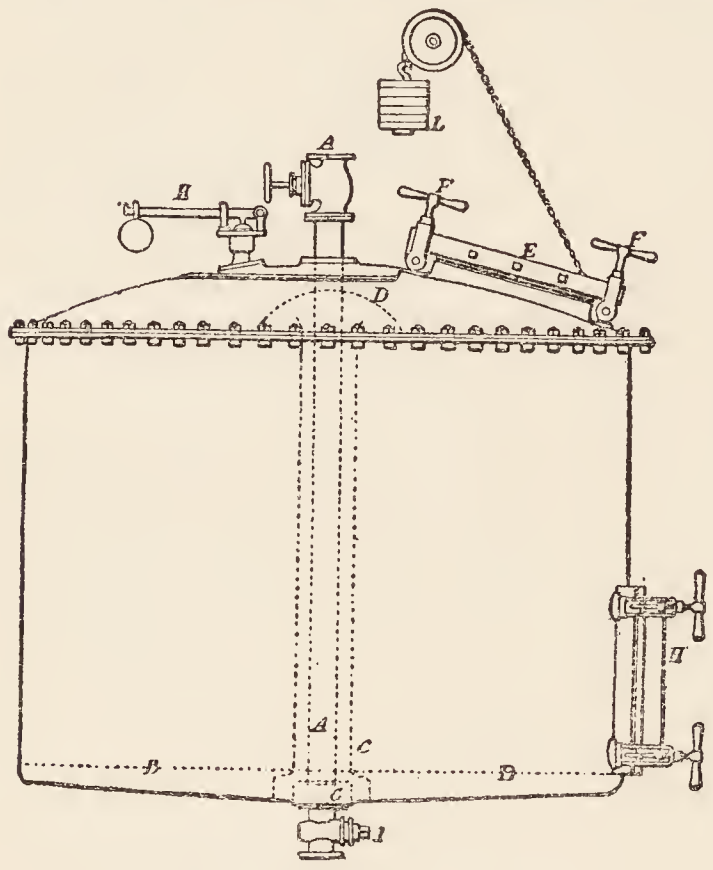


FIG. 1.

false bottom B, on which the grass rests. Steam enters by the pipe A, which reaches below the false bottom and causes the liquor to rise up the outer pipe C, strike against the 'bonnet' D, and distribute itself over the grass in a fine spray. The door E is for filling in the grass, and the door H for emptying. The boiler is fitted with a safety valve K. Each boiler holds about 60 cwt. of grass, and the operation lasts about five hours. The amount of soda varies according to the nature of the esparto, Spanish requiring less than African: about 16 lbs. of 70 p.c. caustic per cwt. is an average quantity. The steam pressure also varies from 5 lbs. to 45 lbs. per square inch. Occasionally an open boil is used. The modern tendency is to employ the higher pressures, as being more economical of time and soda. Other forms of vomiting boilers have lately been introduced, in which the vomiting arrangements are fixed either outside the boiler altogether, as in Roeckner's, or are placed at the sides, as in Sinclair's, thus giving more space for the grass. The alkali used is invariably soda. The boiling operation being completed, the liquor is run off from a cock at the bottom of the boiler and then pumped to a large store tank for recovery of the soda. In most up-to-date mills it is customary to use wash waters from previous 'boils' to effect a removal of about 90 p.c. of the total alkali used. This is important, because it is desirable that as high a percentage of recovery as possible should be obtained, and yet at the same time obviate the heavy cost of evaporating large quantities of very weak liquors.

The final washing is generally carried out by mixing the unbeaten pulp with water in a 'potcher' fitted with paddles on the system of an ordinary washing engine, and after a suitable beating, it is passed over sand tables and strainers to a stuff chest, where it is finally pumped up to a travelling wire cloth 'presse-pâte system,' or through a concentrator, whereby the remaining soluble alkaline products are removed.

Similar in principle is the cone breaker system, Cornett's, whereby the pulp from the boilers is passed through a cone breaker before passing through the strainers. An improvement is claimed for this process in a better separation of the knots from the fibre.

Both systems involve a large space for their proper working, but do away with a great deal of labour.

The washing engine, which may be used for any other fibres besides esparto, is shown in Fig. 2. It consists of a rectangular vessel with rounded ends, in the centre of which is the mid-feather B. The action of the roll A, which is fitted with clusters of steel knives G, disintegrates the grass and causes it to circulate round the engine. The floor is sloped as shown by the dotted lines D and D′, the effect being to cause the grass to pass under the roll A, the knives of which pass close to similar stationary knives fixed to the 'bed-plate' I. The distance between the roll and the 'bed-plate' can be varied at will by means of the wheel E.

A continuous stream of water is run into the engine, and the dirty water is lifted by means of the 'drum washer' C, the periphery of which is covered with fine wire gauze. The centre of the drum is formed of a conical tube the narrow end of which is towards the 'mid-feather.' The dirty water passing through the wire gauze is lifted by the bucket-like compartments C, and is discharged through the centre of the drum, whence it is led away by the trough L, and passes down the 'mid-feather,' which is made hollow for the purpose.

The grass having been thoroughly washed and reduced to the state of pulp by means of the steel knives in the roll, is ready for bleaching. This operation will be described subsequently.

(*c*) *Straw boiling.* Straw closely resembles esparto in its chemical characteristics, but being more highly lignified a somewhat severer treatment is required. This is obtained either by boiling at a very high pressure, 60–80 lbs., or by using a larger proportion of caustic soda (18–20 lbs. per cwt.). In treating straw for use in high-class papers, it is customary to blow it through a large receptacle, the floor of which is covered by a sieve kept in vibratory motion. The receptacle is arranged that heavy particles, such as sand or stone, fall through the grid in

the first section, while the heavier particles of straw, such as the knots, are carried forward to the second section. The very light pieces are carried through to the third section.

The advantages of this system of treatment are, that the subsequent operations can be conducted with greater uniformity. The boiling operation usually takes place in large revolving boilers. Owing to the rotary action of the boiler, the straw is in the state of fine pulp and readily flows through a 3-inch pipe. It is run into tanks, the bottoms of which are formed of perforated tiles. The liquor is run off and fresh water added until all soluble matters have been removed. It is then ready for bleaching.

In making straw pulp of fine quality it is sometimes found advantageous to pass the washed pulp between horizontal revolving stones, whereby the knots and any unboiled portions are finely ground and rendered more easily bleached.

(*d*) *Wood v.* Cellulose.

(*e*) *Other fibres.* There are a number of fibrous materials which are available for the paper-maker, such as jute, manilla, adansonia, &c., the treatment of which calls for no special notice. The nature of the treatment which they undergo varies with the kind of paper for which they are intended. The greater number of such fibrous materials are used for papers where strength is of far greater importance than colour or appearance, such, for example, as brown papers and packing papers. In such cases the paper-makers aim at a minimum resolution of the fibre, so as to preserve the strength and increase the yield.

The cheapest method of preparing such fibres is to boil them under pressure with milk of lime. This treatment is not so effective as that with caustic soda.

There is another very important material which may be mentioned here, viz. mechanical wood-pulp. A large quantity of this is used in the cheaper kinds of paper. It is prepared by

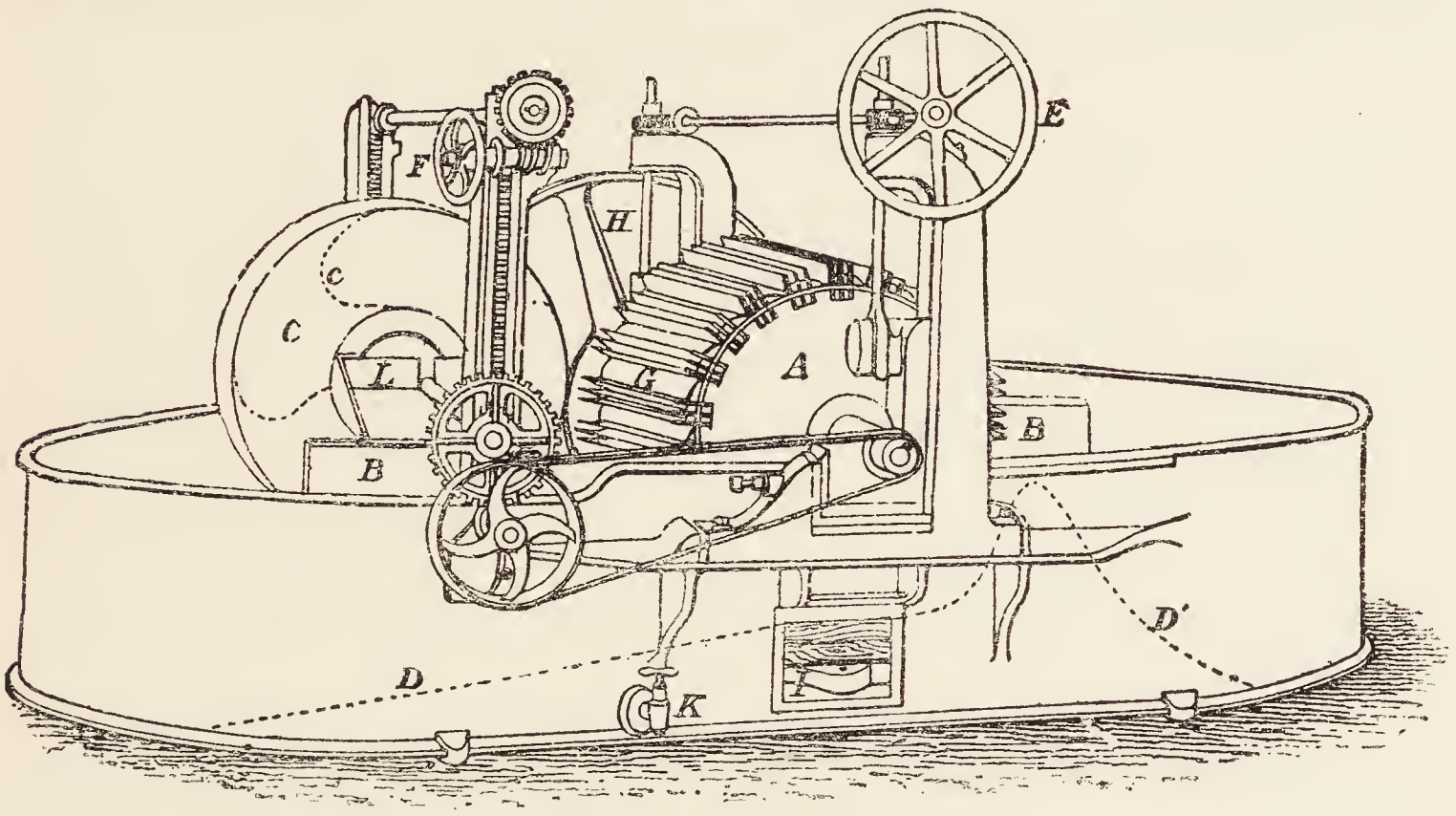


Fig. 2.

disintegrating wood by mechanical means alone. Blocks of wood, from which the knots have been removed, are pressed against revolving stones; at the same time a stream of water flows on to the stones. The wood is so placed that the fibres are torn off in the direction of their length in order to secure as great length as possible. The stream of water carries the pulp forward as fast as it is made. The larger undisintegrated portions are removed by screens of coarse wire cloth. In order to still further refine the pulp it is caused to pass between two horizontal cylinders of sandstone, the upper one of which revolves rapidly.

Where power is cheap such pulp can be economically prepared; it is, however, at best but a poor substitute for esparto and other pulps. Paper made with it has but little strength, and is very susceptible to atmospheric action. The woods chiefly used are white pine and aspen; the latter yields a pulp of good colour but little strength.

3. **Bleaching.** The processes of bleaching paper-pulp are practically identical for all classes of material. The agent employed is a solution of calcium hypochlorite, made by dissolving bleaching-powder in water. The operation may be conducted in the breaking engine previously described, or in a separate engine called a 'potcher,' which is similar in construction, but the roll is furnished only with blunt blades, which serve as paddles to cause the pulp to circulate. Sometimes large potchers made of brick and cement are used.

A system that is being very largely used, is that known as the 'Continuous Bleaching Process,' where the bleaching is carried on in a series of towers (*v.* Fig. 3). The pulp, after washing and breaking, is pumped into the first tower, and after partial removal of the water by means of a concentrator, is bleached while being kept in circulation by means of a centrifugal pump placed at the base of the tower. If only one tower is in use, the stuff can be pumped up continuously to the top of the tower, where it is distributed by means of a cone towards the sides.

Where there is a series or ' battery ' the pulp is pumped up into the next tower, and so on through the series. It is usual to have a second concentrator fitted to the last tower for the purpose of removing the spent bleach, and the soluble non-cellulose constituents.

The advantages claimed for this system are (1) comparatively little power is required for circulating the stuff, (2) an approximate saving of bleach, equal to 25 p.c. owing to the concentration of the pulp under which the bleaching process is carried out, (3) the bleaching is carried out at the ordinary temperature, thus obviating any possibility of tendering the pulp.

The action of the calcium hypochlorite may be hastened by heat, the ' potchers ' being provided with steam pipes for this purpose, or by the addition of sulphuric or hydrochloric acids. The best results are obtained by the action of bleaching solution alone, in which case a longer time must be given. This is more than compensated for by the extra yield of pulp and its greater strength.

The amount of bleaching-powder necessary to bleach well-boiled pulps varies from about 7 p.c. in the case of straw and "easy-bleaching" wood pulps to about 15 p.c. in the case of harder wood. These amounts are calculated on the unboiled materials.

Chlorine gas as a bleaching agent was formerly used for rags, but is now almost entirely superseded. As a matter of fact, chlorine will not bleach the majority of pulps ; it enters into combination with the fibre substances, producing yellow-coloured chlorinated products. Advantage has been taken of this fact by F. C. Glaser in his process for treating straw. The straw is first boiled with a reduced quantity of soda ; it is then drained and exposed to the action of chlorine gas. A subsequent treatment with bleaching liquor produces a very pure white pulp.

The bleaching of pulp by means of the products of the electrolysis of chlorides has attracted much attention. Of the processes introduced, one of the earliest, which was more or less successful, is that of M. Hermite, who electrolysed magnesium chloride. Various other systems have been devised, using common salt as the electrolyte. The usual method in these systems

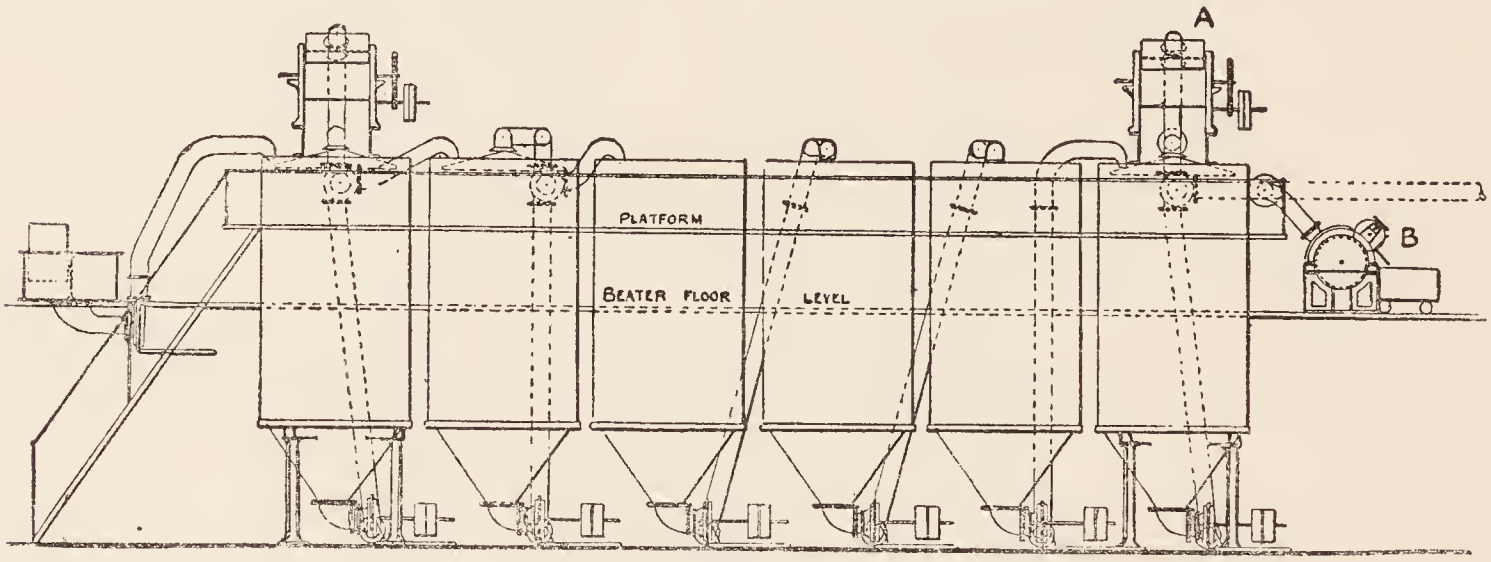


FIG. 3.

is to allow the products of electrolysis, namely, chlorine and caustic soda, which are formed at each pole of the cell, to interact, forming sodium hypochlorite and common salt. The bleaching activity of sodium hypochlorite is certainly greater than that of calcium hypochlorite for the same chlorine strength, and has the added advantage that on reduction of the hypochlorite a more stable compound is formed, namely, sodium chloride, which can be easily removed by washing. Such a system can be worked as economically as ordinary bleaching powder for certain chlorine strengths, and is certainly cleaner to work. But it has one great drawback, namely, that since the optimum concentration of chlorine is only about 10 grams Cl per litre, it involves the use of a very large number of cells to produce enough hypochlorite to bleach sufficicnt material for a mill with, say, an ouptut of 100 tons per week.

The electrodes in the different systems vary. The upkeep of the electrolytic cells is very heavy unless platinum be used. In this case it is a question of initial cost, apart from cost of electrical power, and the user naturally takes this into consideration.

After bleaching, and before the next operation of beating, the pulp is sometimes purified by passing it over a ' presse-pâte,' which consists of a strainer and that part of a paper machine on which the web of paper is formed. The pulp is thus made into a thick continuous sheet ; at the same time all soluble impurities, such as calcium chloride, &c., are removed.

The ' presse-pâte ' system has latterly been largely superseded by the use of ' concentrators ' such as the ' Couper ' concentrator.

This consists of a revolving drum fitted with a central cone arranged so as to deliver water at both ends. The drum is of perforated brass and covered with wire-cloth. The pulp is pumped through a butterfly throttle valve into a splaying mouth, whereby it is caused to flow along the whole width of the drum cover. Thc cover or hood is so arranged by means of packing, that the water in the beaten stuff can be forced through the wire-cloth of the revolving drum, at a pressure of 2–3 lbs. to the square inch, leaving a mat of fibre upon it. The fibre is then picked off the wire by means of a jacketed couch roll, and again removed by means of a wooden doctor, and deposited into boxes.

This action secures a higher concentration of pulp than the ' presse-pâte,' as in the latter case the water is separated from the fibre by gravity only.

4. Beating. The bleached pulp, before being made into paper, requires to be beaten up into fragments of from 1 to 2 mm. in length. In the case of esparto, straw, and wood, this length represents that of the individual fibres; the beating operation, therefore, is confined to completing the disintegration produced by the boiling and bleaching processes. But in the case of cotton and flax, the individual fibres of which are about 30 mm. in length, a much more extended mechanical treatment is necessary. The operation is conducted in an engine called the 'beating engine' similar in construction to the breaking or washing engine already described (Fig. 2), the only important difference being that the roll of the former is furnished with a larger number of knives, which are usually thinner across the face and sharper.

The distance between the roll and the bedplate is arranged so as to 'tear' the fibres, instead of 'cutting' them, so as to give them the maximum amount of felting power. In some cases the knives are made of bronze in order to avoid contamination of the paper with iron-rust. Various other forms of beating engines have lately been introduced which differ somewhat in the arrangement of the various parts, but which do not call for special notice.

It is in this stage of the treatment of the pulp that the various loading, sizing, and colouring materials are added. Before doing this, however, it is necessary, unless the operation has been previously performed in the washing engine, to remove the excess of bleaching solution. This may be done by simple washing, many beating engines being provided with washing drums for the purpose; or the bleach may be neutralised by the addition of an antichlor, such as sodium sulphite.

5. Loading. Most papers, except perhaps the very finest 'writings,' contain some added mineral matter, such as 'pearl-hardening' (calcium sulphate, ground or precipitated) for the better qualities, and china clay for the cheaper papers. This addition cannot, unless carried to excess, be considered an adulteration, as it fills up the pores of the paper, and enables it to take a better surface under the calender.

The object of loading is not primarily that of giving weight to the finished paper but to produce certain characteristic effects, and in that sense therefore the term 'loading' is a misnomer. Opacity, softness, grain of surface, absorbency for ink, are produced by the use of various loadings. The usual mineral loading is china clay, but pearl hardening, *i.e.* calcium sulphate, mineral white, barium sulphate (ordinary and artificial) are frequently used. As an example of an organic filler, dry starch may be taken, but this also acts somewhat as a sizing agent.

Sizing. All writing papers, and most printing papers, require to have some material added to them that will enable them to resist ink. This can be done in two ways—viz. by engine-sizing and tub-sizing: the former is done in the engine itself, the other in the finished paper. Engine-sizing consists in the addition of resinate of aluminium, which is precipitated in the pulp by the mutual decomposition of resinate of sodium, prepared by dissolving rosin (colophony) in sodium carbonate with a solution of alum or alumnium sulphate. The amount of alum added to pulp is largely in excess of that necessary to fully precipitate the resin; the excess appears to be necessary in order to get a hard paper. It probably has some action on the cellulose itself. The excess, moreover, tends to brighten the colour of the paper.

The operation of sizing in the production of various classes of paper is an important one for the following reasons:—Firstly, the capability of the paper to resist the penetration of ink or, as in the case of artists' papers, water-colours. Secondly, the essentially important character of 'hardening' the sheet, and in this way increasing the toughness and elasticity of the paper. Synonymous with these physical properties would be the capacity of the fibres constituting the sheet to resist wear and tear, thus permitting of a great deal of handling. Sizing, therefore, simply consists in filling up the air spaces, and at the same time cementing the 'felted' fibres together by some suitable ink-resisting medium, *i.e.* rosin soap or a gelatinous compound such as cellulose hydrates, starch, gelatine, etc., or mixtures of the latter with rosin.

Such an effect can also be obtained simply by the operation of beating, for it is undoubted that the cellulose complex is itself an instance of a solution of a solid, and therefore under such internal stresses as would be set up under the 'beating' would naturally tend to revert to a liquid phase by the combination of the cellulose with water to form cellulose hydrates. This is clearly seen in grease-proof papers, where the paper is quite impervious to oil, ink and water, such an effect having been produced solely by beating the cellulose for several hours to such a point of hydration that it passes almost into a gelatinous condition.

Tub-sizing. This consists in passing the finished paper, either in the form of sheets or in the web, through a solution of gelatin to which alum has been added. Occasionally soap is added to the gelatin. When alum is added to a solution of soap and gelatin, the soap is decomposed and an infinitely fine precipitate is produced, which forms with the gelatin a kind of emulsion. The addition of the soap enables the paper to take a high surface with a minimum of pressure under the calender. Latterly a new form of soluble starch containing a certain proportion of starch acetates to replace gelatine has been used with success.

6. Colouring. In highly bleached pulps, especially of the natural oxycellulose type, there is a tendency to revert to a slightly yellowish tinge when dried over the steam cylinders. To correct this it is customary to add complementary colours—reds and blues. The blues usually employed are aniline blues and ultramarines. The reds are either alizarin lakes or other synthetic dye-stuffs.

'Toned' papers are sometimes made by colouring a fully bleached pulp with soluble iron salts. This system is based on the fact that the basic iron salts acting catalytically as a conveyer of oxygen tend to convert the cellulose into oxycellulose. The brittleness observed in old papers is due to this oxidation, hence it is advisable to keep as far as possible to such conditions as would reduce oxidation to a minimum.

For this reason, therefore, it is far preferable to use 'self-toned papers,' *i.e.* papers which have been prepared from pulps which have only been bleached to the desired colour, and usually termed a 'three-quarter bleach.'

Coloured papers are prepared by dyeing directly in the engine with the various substantive acid and basic dye-stuffs of the colour required, the two latter groups of adjective dye substances being respectively precipitated by the alumina radical of the alum or the acid radical of the same salt.

In high-grade papers, where depth of colour is not so essential as fastness to light, acids and alkalis, various 'vat colours,' *i.e.* lakes of the naphthol and anthracene series, are used, such lakes being fixed in the pulp by means of soap and alum or resin size and alum.

Vegetable dyes, as for example, logwood or catechu, are now very seldom used, but various pigments, organic and inorganic, find great application in colouring pulp. Among these may be mentioned Prussian blue, lead chromate, iron oxide, salts, and ultramarine.

7. **Making into paper** (*Hand-made paper*). This is made on a mould of wire-cloth, furnished with a movable frame of wood called a 'deckle,' extending some distance above the surface. The workman dips the mould with its 'deckle' into a vat containing the beaten pulp largely diluted with water, and removes more or less pulp, according to the thickness of paper required. He, then, by dexterous lateral movements causes the fibres to unite and form a continuous sheet; at the same time the excess of water drains away. The 'deckle' is then removed, and the wet sheet of paper transferred to a piece of felt. This operation is continued until a number of sheets of paper and pieces of felt have accumulated, forming what is called a 'post.' They are placed in a press to remove a further quantity of water, and are subsequently dried. The sheets are then passed through a solution of gelatin, and hung up on lines or poles to dry. When dry the sheets are calendered.

Comparatively little paper is now made by hand on account of the great expense of labour; it is, however, perferred for bank-notes, drawing-paper, &c., on account of its uniform strength. Owing to the fact that a shaking motion in every direction can be given to the mould, the fibres are irregularly distributed, and the maximum of felting power is obtained, whereas in machine-made paper, as will be seen subsequently, the fibres tend to place themselves in the direction in which the stream of pulp flows. For the method of manufacture of hand-made filter paper, *see* J. Barcham Green, J. Soc. Chem. Ind. 1920, 40, 100 R.

Machine-made paper. The modern Fourdrinier paper machine, so-called from the original inventor, consists essentially of an endless mould of wire-cloth on to which a continuous stream of pulp flows and on which a continuous sheet of paper is formed. On leaving the wire-cloth the wet sheet of paper passes through a series of rollers and over heated cylinders and calenders whereby it is dried and finished. The machine is shown in side elevation, Figs. 4 and 5.

The pulp on leaving the beaters flows into a large store vessel called a stuff-chest, where it is diluted to the proper consistency with water. It is furnished with agitators to keep the pulp uniformly distributed. From here it is pumped and delivered under a constant head, to the sand tables. These consist of a long series of shallow troughs, the bottoms of which are covered with pieces of felt or thin strips of wood placed across the direction of the stream of pulp and at a slight angle, the object of which is to retain any particles of sand or dirt. The pulp passes from the sand tables to the strainers, which are usually of the revolving type, and like the old flat type of jog strainer or knotter consist of strong bronze plates having a large number of fine V-shaped slits cut in them. The slits are from 2 to 3 inches long, and vary in width from 1·007 to 1·05 of an inch. These slits allow only the fine fibres to pass, retaining all unboiled or unbleached portions of fibre or other impurities. The passage of the stream of pulp through the slits is assisted by giving a vigorous shake to the strainer plates or by means of a pump placed below. One of these strainers is shown at *c*; the shake is produced by the cam *a* acting on the hammer *b*.

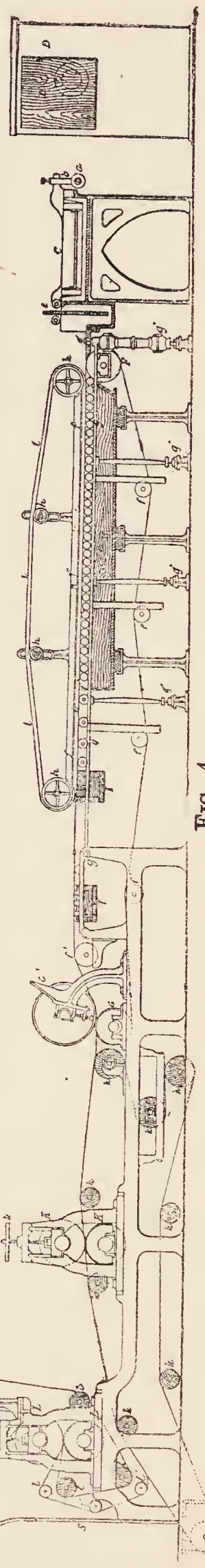


Fig. 4.

The strained and purified pulp passes from the strainer on to an endless travelling wire-cloth which is carried by a large number of small rolls *f″* and by the large rolls F*f′* and G. The amount of pulp flowing, and consequently the thickness of the finished paper, is regulated by the sluice *e*. The thickness also depends upon the rate at which the wire-cloth travels; it may vary from 60 to 600 feet per minute.

Travelling with the wire-cloth are two endless thick india-rubber bands *i* called 'deckle straps.' These can be regulated at any distance from each other and serve to determine the width of the sheet of paper. The rolls *f″* and the wire-cloth are carried by standards *g″*

which are joined at their lower ends. At the top they are connected with a rod having a rapid to-and-fro motion which is communicated to the wire-cloth. This shaking motion serves to some extent to neutralise the tendency of the

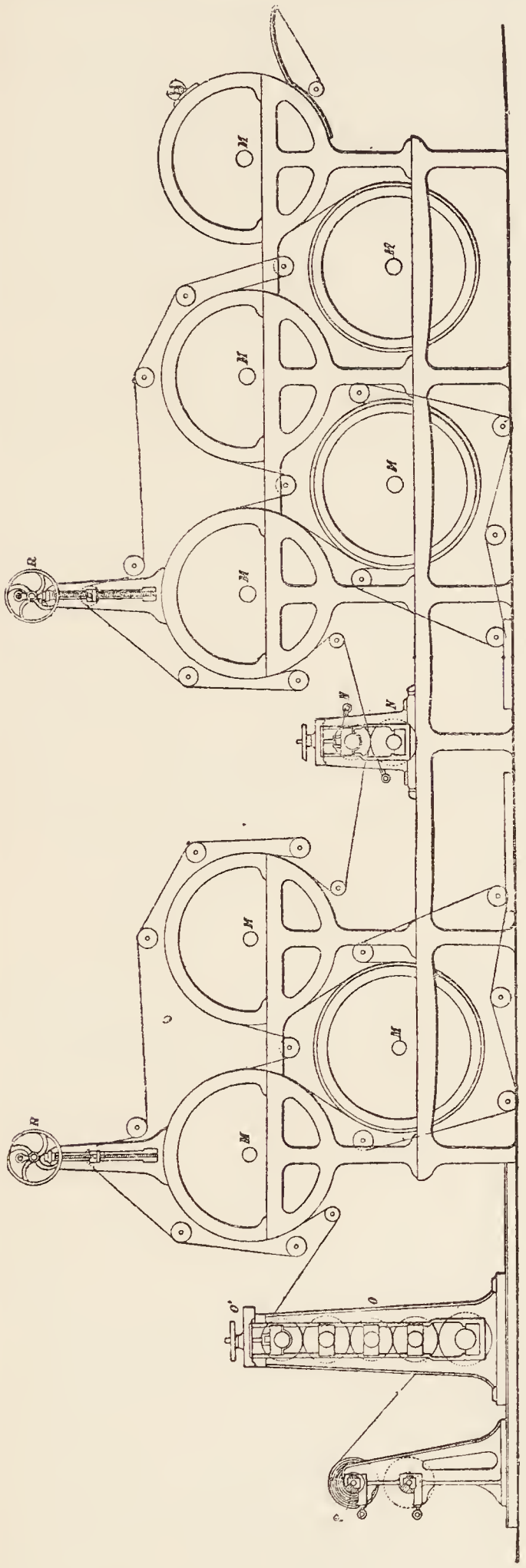


Fig. 5.

fibres to set themselves in the direction of the flow of the pulp.

The small rolls *f''* cause the excess of water to pass more freely through the wire-cloth. As the sheet of paper passes along, it goes over the vacuum boxes I which are connected with air-pumps, by which a further quantity of water is removed from the sheet of paper.

Underneath the wire-cloth is a box K called a 'save-all.' The water passing into it holds in suspension a certain amount of fibre. This fibre can be recovered by passing the water through a filter or the water may be used to dilute a fresh quantity of pulp. Any pattern, or 'water-mark' as it is called, may be produced on the paper by causing a light skeleton roll, called a 'dandy roll' covered with raised wire in the form of the pattern required, to press lightly on the wet paper. It is generally placed between the vacuum boxes I. After passing the last box I the still wet paper passes between the 'couch rolls' GG'. These are covered with felt and serve by their pressure to still further dry the paper. The paper here leaves the wire-cloth and is transferred to an endless felt which travels in the direction of the arrows over the roll *k*. On its journey, it passes between the 'first-press rolls' K, and then through the 'second-press rolls' L. The paper, being still weak, is supported by a felt travelling on the rolls *l*. After leaving the 'second-press rolls' L, the paper is carried to the drying cylinders M, heated with steam, of which there may be as many as twelve or more.

They are generally divided into two sets, between the sets being a pair of highly polished heated rollers N called 'smoothers.' After leaving the last drying cylinder the paper passes through the calender O and is then wound off at P.

Single-cylinder machine. In the single-cylinder or 'Yankee' machine, the paper after having been formed on a wire cloth in substantially the same manner as in the Fourdrinier machine, is dried by passing over one very large cylinder.

In another form of machine the paper is formed on the periphery of a cylinder covered with wire cloth, which revolves in a vessel containing the pulp.

Calendering. It is sometimes necessary to give a greater 'surface' to a paper than is acquired by the calender at the end of the machine. This may be done in several ways. One method, called 'web-glazing,' is to pass the web of paper between alternate rolls of polished iron and highly compressed cotton or paper. Another method, called 'plate-glazing,' consists in passing a bundle of sheets of paper alternated with polished zinc or copper plates, between a pair of rolls to which great pressure is applied.

Still another method, which is known as 'friction-glazing,' is to pass the web of paper between two rolls, one of which travels at a much higher rate than the other. After calendering, the paper only requires cutting and sorting before being placed on the market.

Soda recovery. Formerly, before the introduction of the Rivers Pollution Act of 1876, all liquors in which esparto and other fibres had been boiled were thrown away; it is now the practice to recover the soda contained in them by evaporating to dryness and incinerating the residue, thus obtaining the soda in the form of carbonate. This has in most cases been found to be highly remunerative. Various forms of apparatus for economically evaporating large quantities of water have from time to time been introduced. These can be divided into two

types, (1) the direct evaporating plants under ordinary atmospheric pressure, and (2) single or multiple effects, where evaporation is carried on under a partial vacuum. A very effective form representing the first type is that known as the Porion evaporator, which consists of a large brick chamber on the floor of which the liquor is placed. A number of rapidly revolving fanners stir up the liquor and distribute it in the form of a very fine spray. The chamber is connected with a reverberatory furnace where the evaporated product is incinerated, the waste heat from which serves for the preliminary evaporation. This evaporator, working with fairly strong liquors, is capable of producing 1 ton of recovered soda for an expenditure of about 27 cwt. of coal.

There are several forms representing the second type, one of the best of which is that known as the 'Scott Multiple Effect Evaporator.' By means of this apparatus, coupled with a rotary furnace, it is possible to effect recovery of 95 p.c. of the soda, and with a coal consumption equal to 10 cwt. per ton of ash produced.

One form of the evaporating plant is shown in Fig. 6, and may consist of one or more vessels. Each unit consists of an evaporator, the heating surface of which is in the form of tubes of two different diameters so arranged that the liquor which circulates in these tubes does so with considerable velocity, thus exposing a large heating surface. The steam generated in the first effect, working under a pressure of 4–5 lbs., is used to heat the second 'effect' which works under a slight vacuum, and so on for each consecutive unit, with a correspondingly increased vacuum.

The 'black' liquor is supplied to the first 'effects' and passes gradually through each succeeding 'effect' until it becomes so concentrated that it will only just flow.

The concentrated liquor is pumped up to a stone tank mounted above a roaster, which may be of the flat hearth type or better still, a rotary

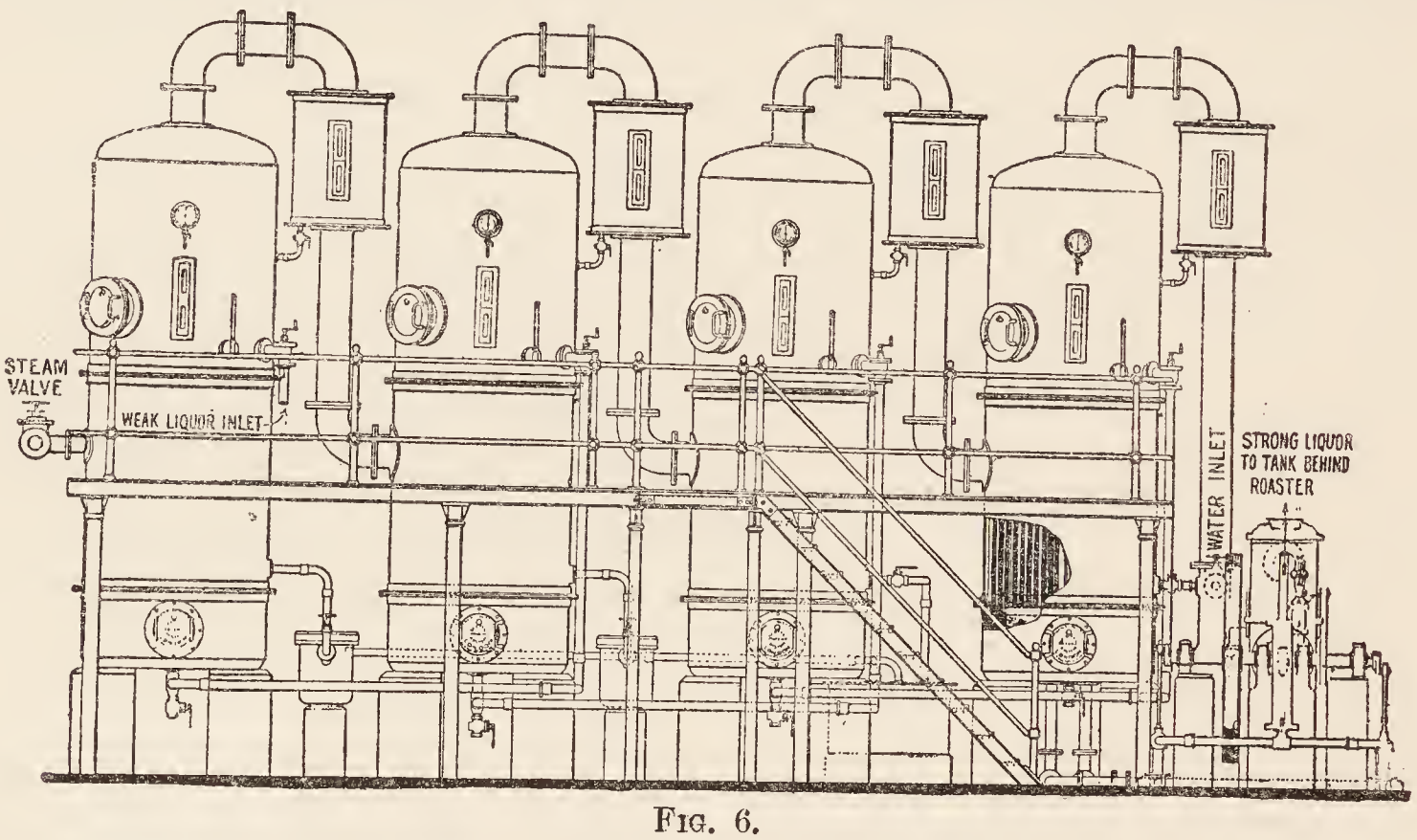


FIG. 6.

roaster. The latter is a revolving steel shell provided with steel rails, and supported on steel wheels, some of which act as 'supports' and others as dividers. The inside lining of firebrick is so arranged that a slight slope is given from the feeding end to the discharging end. The concentrated liquor is fed into the roaster at a constant rate, the temperature of the roaster being at white heat. This causes immediate evaporation and firing of the organic matter. The fused sodium carbonate is carried forward to the end of the roaster, and is ultimately discharged as a dark incandescent mass into barrows placed at the end of the furnace. The contents of the barrows are left to burn slowly when the product is almost quite white.

The Yaryan evaporator is similar in principle to that already described. An important advantage of these evaporators is the fact that the liquors, excepting while in the incinerating furnace, are not in contact with the products of combustion of the fuel employed. Moreover, the bulk of the water evaporated is recovered in the form of distilled water.

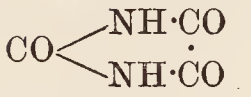
The recovered soda, which, as has been said, is in the form of carbonate, may contain in addition a considerable quantity of potash, derived from the fibrous substances which have been boiled in it; also in the case of straw or esparto, a large proportion, as high as 7 p.c., of silica. It is dissolved in water and causticised by boiling with lime, when almost the whole of the soda it contains is recovered in the form of sodium hydroxide. It should be borne in mind, however, that it is liable to contain various accumulated impurities such as sulphate and chloride, &c., derived from the soda originally employed, and from that which has to be added to make up the loss in evaporation. This loss, together with that due to soda retained in the fibre, leakage, soda volatilised during calcining, and soda left in the lime mud after causticising, invariably amounts to 5–10 p.c.

It is important that the loss should be made up with as pure a form of alkali as possible.

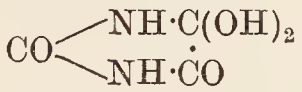
E. J. B. and W. B.

PAPER-COAL. A synonym for Dysodile (*q.v.*).

PARABANIC ACID (*Oxalylcarbamide*)



prepared by the oxidation of uric acid with moderately concentrated nitric acid (Liebig and Wohler, Annalen, 1838, 26, 285; Strecker, Annalen, 1861, 118, 151; Tollens, Ber. 1872, 5, 801; Behrend and Asche, Annalen, 1918, 416, 226), with hydrochloric acid and potassium chlorate, with manganese dioxide and hot dilute sulphuric acid, or with bromine and water; or by oxidising guanine with hydrochloric acid and potassium chlorate (Fink, Annalen, 1864, 132, 298); has been synthesised by heating oxamide with phosgene at 170°–180° (Basaroff, Ber. 1872, 5, 477), or by boiling it with phenyl carbonate (Cazeneuve, Compt. rend. 1899, 129, 834); by the action of phosphoryl chloride on a mixture of oxalic acid and carbamide, or on oxaluric acid (Grimaux, *ibid.* 1873, 77, 1548); by distilling the monoureide of nitropyruvil $C_4H_3(NO_2)N_2O$ with bromine and water (Grimaux, *l.c.*; 1874, 79, 1478); and by the action of oxalylchloride on carbamide in ethereal or acetic anhydride solution (Biltz and Topp, Ber. 1913, 46, 1387; Bornwater, Rec. trav. chim. 1912, 31, 105). This method does not give so good a yield of the acid as the older methods, but is recommended for the preparation of substituted parabanic acids. Parabanic acid crystallises in flat, monoclinic prisms, soluble in 21·2 parts of water at 8°, and melts and sublimes at 100° (*cf.* Biltz and Topp (*l.c.*), who give m.p. 242°–244°); the smallest trace of impurity lowers the melting-point considerably. The *hydrate* $C_3H_2O_3N_2,H_2O$ or



is obtained when uric acid is oxidised with nitric acid (sp.gr. 1·3) at 35°–60°, it forms large compact crystals, soluble in 7·4 parts of water at 8°, becomes anhydrous at 150°–160°, and the dried substance recrystallises from water in anhydrous needles (Tollens and Wagner, Annalen, 1873, 166, 321; Tollens, Ber. 1872, 5, 801; Annalen, 1875, 175, 227). Parabanic acid has heat of combustion +212·7 Cal., heat of formation +139·2 Cal., heat of dissolution −5·1 Cal. at 20° (Matignon, Compt. rend. 1891, 113, 198); the dissociation constant for N/32 solution is $0{\cdot}75\times10^{-6}$ (Wood, Chem. Soc. Trans. 1906, 1835). In diazo acetic ester solution the dissociation constant $K=0{\cdot}04025$, $C_H=0{\cdot}001045$, (Calcagni, Atti R. Accad. Lincei, 1916, [5], 25, i, 643); *v.* Paterno (Gazz. Chim. ital. 1914, 44, i. 241) for the action of ammonia on the acid in presence of light. In its physiological action parabanic acid resembles alloxan; it is eliminated in the urine partly unchanged and partly as oxalate (Pohl. Zeitsch. exper. Pathol. u. Ther. 1910, 8, 308); it acts on the central nervous system, producing first stimulation, then paralysis, and finally kills in a state of torpor (Lusini, Chem. Zentr. 1895, ii. 311, 727, 838). For the metabolism of parabanic acid *v.* Lewis (J. Biol. Chem. 1915, 23, 281). Parabanic acid is a dibasic acid, the *ammonium* $C_3HO_3N_2(NH_4)$, *potassium* $C_3HO_3N_2K$, and *sodium* $C_3HO_3N_2Na$ *salts*, prepared by adding alcoholic ammonia or potassium or sodium ethoxide to an alcoholic solution of the acid, are crystalline precipitates converted in aqueous solution into the corresponding salt of *oxaluric* acid $H_2N{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CO_2H$; the *mono*-$C_3HO_3N_2Ag,H_2O$, and *di*-$C_3O_3N_2Ag_2,H_2O$ *silver salts* exist (Menschutkin, Annalen, 1874, 172, 73; Rudinskaia, J. Russ. Phys. Chem. Soc. 1885, 278); the *carbamide salt*

$$C_3H_2O_3N_2,CO(NH_2)_2$$

forms flat prisms (Hlasiwetz, J. pr. Chem. 1856, [i.] 69, 106).

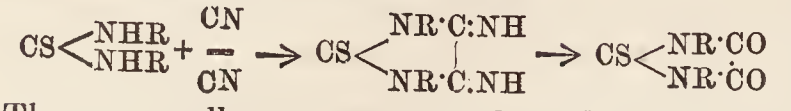
Alkyl and **aryl substituted parabanic acids** have been prepared by the oxidation of certain purine derivatives, or more generally by the action of alcoholic silver nitrate on the corresponding thioparabanic acid. These compounds do not yield a precipitate with a cold solution of calcium chloride to which ammonia has been added, but on warming the mixture, calcium oxalate is precipitated (Andreasch, Ber. 1881, 14, 1447; 1898, 31, 137). *Methylparabanic acid* $C_3HMeO_3N_2$, by oxidising theobromine with chromic acid, or caffeine with bromine, forms transparent prisms, m.p. 149·5°; *v.* Biltz and Topp (*l.c.*), who gives m.p. 153°–154°, b.p. 201°–202°/13 mm.; the *methyl-carbamide salt* $C_4H_4O_3N_2,C_2H_6ON_2$ has m.p. 127°–128° (Maly and Hinteregger, Ber. 1881, 14, 723, 893; Monatsh. 1882, 3, 85; Fischer and Frank, Ber. 1897, 30, 2609). *Ethylparabanic acid* $C_3HEtO_3N_2$, m.p. 45° (*cf.* Biltz and Topp (*l.c.*), who gives m.p. 127°–128°, and different properties); *allylparabanic acid*, m.p. 140°. *Dimethylparabanic acid, cholestrophan* $C_3Me_2O_3N_2$, obtained by oxidising caffeine with nitric acid (Stenhouse, Annalen, 1843, 45, 371; 46, 229), with chlorine water (Rochleder, *ibid.* 1850, 73, 57), or with bromine water, or by the action of methyl iodide on silver parabanate (Andreasch, Ber. 1898, 31, 138); melts at 145·5° and distils unchanged at 275°–277° (*cf.* Biltz and Topp (*l.c.*), crys. in leaflets, m.p. 154°, b.p. 148°–150°/13 mm.); is soluble in 53·4 parts of water at 20° (Maly and Hinteregger, *l.c.*), and its heat of combustion is +539·1 Cal. (Matignon, Ann. Chim. Phys. [vi.] 28, 70). *Diethylparabanic acid* $C_3Et_2O_3N_2$, m.p. 46° (*cf.* Biltz and Topp (*l.c.*), who gives m.p. 49°–51°); *methylethylparabanic acid* $C_3MeEtO_3N_2$, by oxidising ethyltheobromine, m.p. 44°; *methylallylparabanic acid* $C_7H_8O_3N_2$, m.p. 75°; *ethylallylparabanic acid* $C_8H_{10}O_3N_2$, m.p. 66°; *methylphenylparabanic acid* $C_{10}H_8O_3N_2$, m.p. 148°; iso*amylparabanic acid* $C_8H_{12}O_3N_2$, m.p. 106°; iso*amylphenylparabanic acid* $C_{14}H_{16}O_3N_2$, m.p. 85° (Stieger, Monatsh. 1916, 37, 625); *ethylphenylparabanic acid*, m.p. 97°. *Phenylparabanic acid*, m.p. 213°–214°, after softening at 208° (Biltz and Topp (*l.c*); *diphenylparabanic acid*

$$C_3(C_6H_5)_2O_3N_2$$

by boiling dicyanodiphenylguanidine with hydrochloric acid, m.p. 204°; Bornwater (Rec. trav. chim. 1915, 34, 289) describes woolly needles, m.p. 206°–207°; Biltz and Topp (*l.c.*) give m.p. 202°; *di*-p-*tolylparabanic acid* $C_3(C_7H_7)_2O_3N_2$, m.p. 144°; *di*-o-*tolylparabanic acid*; *benzylparabanic acid*, m.p. 167°–169°.

Thioparabanic acids are prepared by passing cyanogen gas into an alcoholic solution of

the thiocarbamide and heating the resulting cyanides with hydrochloric acid.



They are yellow or orange-coloured crystalline compounds, and the thioparabanic acids corresponding with all the substituted parabanic acids described above have been prepared (Andreasch, Ber. 1881, 14, 1447; 1898, 31, 137); Biltz and Topp, *l.c.*). M. A. W.

PARACODEIN. Dihydro-codein hydrochloride.

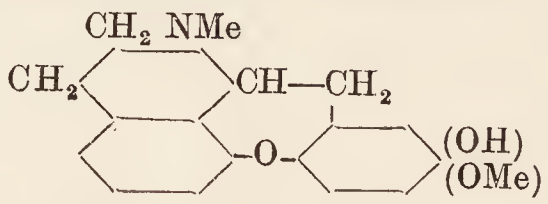
PARADOL. The pungent principle of grains of paradise (*Amomun melegueta*). Yellow oil, sp.gr. 1·069 at 20°/20°. $[\alpha]_D = +9{\cdot}2$, $n\frac{20}{D} = 1{\cdot}5232$. Contains 10·93 p.c. of methoxyl. On methylation gives a crystalline product identical with methyl ether of gingerol, and an oil. The main fraction obtained by distilling paradol boils at 230°–234°/8 mm., sp.gr. 10·415/20°, $n\frac{20}{D} = 1{\cdot}5198$. Is optically inactive and does not give a crystalline methyl ether. The pungency of paradol is only slightly affected by boiling with alcoholic potash, whereas that of gingerol is practically destroyed (Nelson, J. Amer. Chem. Soc. 1917, 39, 1466).

PARAMORPHIN. Dihydro-morphin hydrochloride.

PAREIRA ROOT. The root of *Chondodendron platyphyllum* contains alkaloids, hitherto known as *bebeerines*, but which are now recognised as different from those obtained from the bark of *Nectandra Rodiaei*, the so-called bebeerin tree. *Iso*-chondodendrine (and probably α- and β-chondodendrine) has the composition

$$C_{18}H_{19}NO_3$$

and has probably the configuration



(Faltis and Neumann, Monatsh. 1921, 42, 311).

PARABISMUT *v.* SYNTHETIC DRUGS.

PARACONIC ACID *v.* LACTONES.

PARAFFIN. *Properties.*—Paraffin is a solid wax-like substance, colourless, tasteless, and odourless, composed of saturated hydrocarbons of the series C_nH_{2n+2}. In the market it is obtained with m.p. from 100°F. (38°C.) to over 135°F. (57°C.). The higher melting varieties are hard and tough at ordinary temperatures; all are plastic for some interval under their melting-points, and when fused are thin mobile liquids. Paraffin expands considerably in melting. With a wick it is easy to get it to burn with a clear white smokeless flame; but it does not burn readily in the mass. Its flashing-point is over 350°F. (177°C.).

The sp.gr. varies from 0·790 to 0·940 according to melting-point and origin. A sample with m.p. 38°C. had sp.gr. 0·8740 at 21°C., and the sp.gr. in the melted state, calculated to 21°C. was 0·795 (Beilby). The specific heat is 0·694. It is a nonconductor of heat and electricity. It contains carbon about 85 p.c., hydrogen 15 p.c. It is insoluble in water, but soluble in ether, mineral spirit and carbon disulphide. It is characterised by indifference to many reagents, and can resist the action of many of the strongest chemicals even when heated.

Uses.—The harder paraffin is used in vast quantities for candle-making; the softer quality for miners' lamps, and household-, ship-, and hand-lamps; also for dipping the sticks of matches in place of the sulphur of long ago; and often gets the name of match or miner's paraffin. The peculiar properties of paraffin make it a useful material for many purposes, and as time goes on it tends to get more plentiful and of lower price, and its applications are extending. It is used for waterproofing cloth, leather, walls, cartridges, and wrapping paper; for coating the inside of vessels to prevent the wood giving a taste to the delicate substances in them, such as butter, mineral waters, beer, &c.; for coating metals to prevent rust and decay; for electrical insulation; for splints in surgery, as a medium for salves, for extracting perfume from flowers; for waxing thread, floors, &c., for heating-baths in laboratories, and numerous other purposes.

Production.—Paraffin is found native in various forms in the coal and other measures, *e.g.* as ozokerite (*q.v.*). A hundred years ago and more Uphall Parish and neighbourhood was lighted with ozokerite candles from Binny quarry, and these were perhaps the first paraffin candles to be used. Galician ozokerite is refined and sent into the market as ceresin. Paraffin was first produced in quantity from bituminous shale, and that is still an important source in Scotland, France, and Australia. In Germany it is obtained from the distillation of brown coal. It is now obtained from American, Galician, and other petroleums, but not from that of Baku. In shale oil and petroleum it is associated with liquid and gaseous members of the paraffin and other series of hydrocarbons. Scotch crude oil contains 11 p.c. of solid paraffin, brown coal tar 12 p.c., Galician petroleum 5 or 6 p.c., American 2 or 3 p.c., Upper Burmah and Assam sometimes 12 p.c. or more. For many years Scotland, with a yearly production of 20,000 tons, was the principal producer in the world, but now America produces 100,000 tons, and Galicia, before the world war, put on the market over 60,000 tons per annum.

Distillation of bituminous shale for liquid products was tried in Scotland by Lord Dundonald as early as 1781, but the world was not ready for it. Previous to 1850 solid paraffin had been extracted in the laboratory from petroleums, wood-tar, and coal-tar, but throughout the world generally it was known only as a chemical curiosity. In France, however, manufacturing it had been attempted on a small scale as early as 1839, and candles proposed and patented in 1845. On the large successful manufacturing scale it was first produced in Scotland from torbanite, and this undertaking at once became well known and influenced the whole world. Later on oil shale was used.

Oil shale is at present worked for oil refining in Scotland, France, and Australia, and shale suitable for the purpose is found in the United States of America, Nova Scotia, New Brunswick, Servia, Spain, Tasmania, and many other places.

In Esthonia there is a successful industry on

an outcrop 50 miles long along the coast, and the shale is also used direct for locomotives and other purposes. Sweden has a works putting through 100 tons a day, and Italy is starting works on its own lines. Germany has shale in several places, and a company started with State support.

There is no hope of the petroleum wells lasting permanently, and the world's stock of it is being rapidly used up. The vast shale fields of the world will before long become of great interest and importance.

The methods of refining are the same for petroleum, brown coal, and shale oils, viz. fractional distillations alternated with treatments of oil of vitriol and of caustic soda; and the heavy oil when it contains solid paraffin, is cooled and pressed for its separation. A description of the Scotch manufacture is so far typical of all, but shale oil requires much more refining than petroleum. Crude petroleum is obtained directly by boring and pumping, whilst shale and brown coal have to be mined and retorted to get the crude oil. This extra expense is to some extent compensated for by the production of ammonium sulphate.

The Shale Oil Industry.

Locality.—At one time there were crude oil works scattered over all the British coal-fields. Now, however, all the oilworks existing in Scotland are situated on a belt of the oil shale formation, 6–8 miles wide, stretching from the shores of the Firth of Forth at Abercorn and Dalmeny 16 miles southward to the west end of the Pentland range of hills at Cobbinshaw. Going due west from Edinburgh for 13 miles lands one in the middle of this tract. Besides this locality there is a regular strike of the shale seams in a narrow strip 10 miles to the east, where the seams lie much closer together. There were workings on it at the village of Pentland. This line is continued to the north side of the Forth and was worked at Burntisland.

The raw material used is a shale, which, while containing not more than 2 p.c. of true bitumen soluble in carbon disulphide, has much organic matter present capable of giving bituminous materials by destructive distillation. It is black or brownish in colour, fine in grain, free from grit, and with brown streak. It is tough, and good samples under the knife curl over in thin shavings, while poorer samples are more friable. Some good foreign shales have not this property of curling in thin shavings. It resists disintegration by weathering. Some shale is 'plain,' having the laminæ parallel with the stratification; other shale is 'curly,' side pressure while plastic having crushed it into wave-shaped, curled irregular masses, with black brightly-polished surfaces. The amount of shale distilled in Scotland in 1916 was 3,009,232 tons, in 1920 2,827,792 tons.

Products.—The crude oil, in amount about 70 million gallons or 273,500 tons per annum in Scotland, varies in proportion of products according to the nature of the shale and the retorting. The principal products are:—

1. Shale spirit or naphtha about 4 p.c. on the crude oil, sp.gr. 0·660–0·750, used as gasolene, motor spirit, solvent for india-rubber, burning in special lamps, &c. Water-white in colour.

2. Burning oil, 20–30 p.c., sp.gr. 0·770–0·830, used for lamps, and for internal combustion engines. Water-white or faint straw tint.

3. Intermediate oil, sp.gr. 0·840–0·865, 10–20 p.c., used for gas-making, gas-enriching, cleaning purposes, oil-engine fuel, grease-making, and fuel for the navy.

4. Lubricating oil, sp.gr. 0·865–0·900, about 20 p.c., used for lubricating machinery. Clear yellow colour.

5. Solid paraffin, 10–12 p.c., *see* above.

6. Still coke, 3 p.c., used as a smokeless fuel for yachts, drawing-rooms, &c., and for electric candles, moulders' blacking, &c. Fixed carbon 95 p.c., ash 0·5 p.c., sulphur 0·4 p.c., volatile hydrocarbons 4 p.c.

7. Ammonium sulphate, about 60,000 tons a year, used as manure, especially for sugar beet growing, and was largely exported.

8. The tars, 15 p.c., washed from the chemicals used in refining, are burned as fuel under the stills, sprayed with superheated steam.

9. Permanent gases are produced in the retorting and used as fuel for heating the retorts; and very rich pure gas is got in the refinery in distilling the crude and heavy oils to dryness and is used for illumination, and for fuel purposes under the stills, and during the war it was used as fuel for motor 'buses. The amount of ammonia recovered in the United Kingdom, expressed in terms of sulphate, in 1921 (Alkali Inspector's Report) was:—

	1921.
Gas works . . .	150,228 tons
Iron works . . .	3,265 ,,
Shale works . . .	35,146 ,,
Coke-oven works . .	56,427 ,,
Producer-gas and carbonising works (bone and coal). . . .	8,187 ,,
Total . .	253,253 ,,

The oil products are composed of the paraffin and olefine series of hydrocarbons with a small but definite admixture of naphthenes and benzenes. In the impurities extracted by the chemicals and the distillation are strong bases of the pyridine and quinoline series, phenols, cresols, pyrene, chrysene, and other hydrocarbons more dehydrogenated than the olefines; but the tars have not been thoroughly investigated.

History.—At Lyon Playfair's suggestion James Young started, in 1848, a works in Derbyshire to refine petroleum from a spring found in connection with coal. The supply, some 300 gallons a day, soon threatened to stop, and Young, who supposed that this petroleum had been distilled by a natural process from the coal, set himself to create artificial petroleum by the distillation of coal at low temperatures. He experimented with many varieties, English and Scotch, and found that cannel or gas coals were suitable. He at last discovered the Torbanehill mineral near Bathgate, which proved exactly what was wanted. He took out his patent for low temperature distillation of

coal in 1850, and the Bathgate works were in operation before the close of the year. Markets were soon created for lamp oil, which was the principal product, and also for lubricating oil and solid paraffin. Young introduced suitable lamps, and paraffin oil rapidly became the light of the people all over Britain. He called lamp oil paraffin oil, and paraffin oil, or simply paraffin, is the name yet commonly given in Britain to mineral oil for lighting purposes, whether of shale or petroleum origin. In America and on the Continent the name paraffin oil is applied to the heavy oil which is pressed directly from the solid paraffin. The manufacture proving a great success a good many works were erected throughout Britain during the run of Young's patent, and many were got ready to start on its expiry in 1864, and others were added afterwards. Factories were also started on the Continent, some of them getting the Torbanehill mineral exported to be distilled abroad. Many works were erected in America to work Young's patent and distil the native coals, and adopted his method of refining. Petroleum from oil springs began to be produced in quantity in Pennsylvania in 1859, and these coal refineries were in existence ready for its refining, and helped in the rapid development of the new industry. Coal oil was already well known in America, and petroleum lamp oil or kerosene is often yet called coal-oil in the States and Canada. In the sixties the exportation of American kerosene to the United Kingdom began and increased rapidly. The lamp oil fell in price from 2*s.* 6*d.* to 1*s.* 3*d.* per gallon, and many works had to stop. In 1871 there were 81 works, within two years only 30. The Americans at first exported only burning oil, and the Scotch modified their retorts to produce heavy oil and paraffin, and bought in American residuum to refine it. Soon the Americans took up these branches, and the United Kingdom was supplied with super-abundance of lubricating oil and solid paraffin, and their prices fell also. The ammonium sulphate, a by-product, became the saving of the industry, and the retorts were so modified that its production was doubled or trebled. About 1880 the supply of Peruvian guano, on which farmers had depended for their supply of combined nitrogen, now began to fail, and as a result the price of sulphate rose to £24 a ton, and the number of works was increased. But by 1880 sodium nitrate was imported in such quantities that the price of ammonium sulphate fell to £8 a ton, while burning oil brought only 6*d.* a gallon; and again there was a collapse. The Russian petroleum industry had developed rapidly after 1873, and through time was competing in the English market for lamp and lubricating oils. Later on came competition from Galicia, Roumania, and the East Indies. The Scottish Industry has thus had many vicissitudes, times of success with expansion alternating with depression and collapse. When bad times came the weaker concerns ceased to exist, but the stronger ones enlarged their works to cheapen production by the many economies that enlarged output makes possible. In the sixty years of the existence of the industry 120 works have dropped out of existence causing the loss of several millions of capital, yet the yearly production has not declined but rather increased. There are now only five companies in all, viz. four with refineries, and one which produces only crude oil and ammonium sulphate. In spite of the increased production of combined nitrogen from many new sources such as iron smelting, mondgas, coal coking, and electrical utilisation of atmospheric nitrogen, the demand of farmers all the world over has increased so that the price of ammonium sulphate remained for a series of years from about £12 to £14 a ton. The war caused a great demand, but export was prohibited and the price to farmers fixed about £16. Twice that sum could have been got abroad. Shales that not long ago would have been rejected as rubbish are now most valuable on account of the large yield of ammonia, and the exhaustion of the shale supply is indefinitely postponed. Recent enlargement of the Scotch refineries, combined with the usual foreign competition, accentuated by the price rivalry between the two great foreign petroleum corporations, lowered the price of the oil and paraffin products before the war in 1914, and the outlook was discouraging. The war created a great demand for motor spirit, fuel oils, ammonia and other products, and the situation was changed. The government and people began to take some interest in the prosperity of this important manufacture. Further economies were necessary, and the combination of all the companies into one organisation was effected. So all the Scottish oil-works are now under one directorate and connected with the great Anglo-Persian company. They get the help of Persian petroleum to keep the works going full.

The continued existence of this home industry has without doubt kept the light of the people at one-half the price of what it would otherwise have been, and a great deal cheaper that it was at the very gates of many American refineries. The intermediate oils between lamp oil and lubricating oil used to be very cheap, sometimes unsaleable and a great expense to store. Ordinary oil engines are made now to burn these oils as satisfactorily as lamp oils, and engines of the Diesel type can use oil of any gravity. So a constant demand and a reasonable price is ensured for intermediate oils, to the advantage of the manufacturer and the country.

Materials that have been used.—Young started the Bathgate works to distil the Torbanehill mineral (torbanite), called also Boghead coal. It yielded 100–130 gallons of crude oil. Volatile matters 65 p.c., ash 22 p.c. It was a rich shale rather than a coal. The residue left from retorting was not a coke as with coal, but was in thin layers like spent shale, and the crude oil was lighter, viz. sp.gr. 0·9, instead of 1·0 as with coal. It was getting exhausted and too expensive within a dozen years, and shales were used instead, and also some parrot coal. The shales at first tried yielded 45–30 gallons a ton, and those now in use give from 30 to 20 gallons. A 30 gallon shale has about 25 p.c. volatile matter and 75 p.c. fixed, of which 5 p.c. is carbon. The shale or parrot coals from the coal measures produced generally a crude oil having a higher sp.gr., more loss in refining, a thinner lubricating oil, and less solid paraffin than the shales of the shale measures.

Geology. The position of the shale measures in Scotland may be seen from the following statement in which the series are arranged in descending order:—

Coal measures proper.
Millstone grit.
Carboniferous limestone series.
Calciferous sandstone series, in which are the true shale measures.
Old red sandstone.

The coal measures proper with their many seams of workable coal have seams of shale or bastard cannel coal which could be profitably distilled in the early bright years of the industry. Over many ordinary seams of coal there was found a foot or more of suitable material which was kept apart and distilled. It was found, for instance, in connection with the splint and Virtuewell coals, the Musselband ironstone, and Kiltongue coal, in the Coatbridge district. Seams from the true coal measures were worked for oil in Fife, Ayrshire, and Midlothian, as well as throughout the English coal-fields in Yorkshire, Lancashire, Cheshire, and Stafford, and in particular there was for some time a considerable Welsh shale oil manufacture at Leeswood in Flintshire. The position of the Torbanehill mineral itself was near the base of the coal measures not far above the millstone grit.

The carboniferous limestone series with its valuable limestone, coal, and ironstone contains seams of shale and parrot coal that were worked for oil in Lanarkshire and Fife.

But foreign competition and low prices caused complete stoppage many years ago of all oilworks in Britain except those of the true shale measures. Cannel coal and the coals allied to it and the shales of the coal and other measures are now expected to be retorted for the purpose of supplying fuel oil for the navy.

The calciferous sandstone series, in its upper division, sometimes 3000 feet thick, contains all the oil shales worked at the present time. The seams, about twenty in all, vary much in thickness and quality in the different districts and the intervening strata are also variable. The following is a generalised section to show the succession, &c. The gallons are the crude oil, and the lbs. the ammonium sulphate, per ton of shale, as obtained in the modern retorts. The thickness in feet.

Hurlet limestone and coal, a widely known position reckoned the top of the shale measures. Strata, 400 ft. blaes, ironstone ribs, blackband ironstone, &c. (containing an upper Raeburn Seam at S. Cobbinshaw 100 ft. above the next shale).

Raeburn shale, 3–6 ft., 40–55 gals., worked at West Calder and Tarbrax. Strata 190 ft., blaes, ironstone bands, &c.

Mungle shale, 2 ft., 35 gals., 30 lbs. Strata 130 ft., blaes, fireclay, ironstone bands, volcanic tuff.

Two feet coal, with a thin *shale* and ironstone band. Strata Houston marls, 230 ft., thick beds, massive, amorphous, unfossiliferous.

Addiewell grey shale, 2 ft., composed largely of entomostraca. Strata 60 ft., blaes, fireclay.

Houston coal, 4–6 ft. Lowest coal that has been worked to any extent in Scotland, Inferior, pyritous, and interbedded with blaes. Strata 150 ft., laminated sandstone, blaes, clayband ironstone.

Fell's shale, 3–7 ft. Principal shale of West Calder district, 26–40 gals., 30 lbs. Strata, Broxburn marl, 135–270 ft., limestone immediately under Fell's shale, 3–6 ft., marly clays, cement stone, no sandstone.

Broxburn grey shale, 6 ft., 23 gals., 35 lbs. Strata 5 ft.

Broxburn curly shale, 5½ ft., 26 gals., 38 lbs. Strata 6 ft.

Broxburn seam, 5–6 ft., 30–35 gals., 40 lbs. At Midcalder there are two other seams above these three Broxburn seams, and another 16 ft. below the Broxburn. Strata 400–500 ft. blaes and marl, then the Binny sandstone, then again blaes and marl.

Dunnet shale, 4–12 ft., 16–33 gals., 24 lbs. At Oakbank there is a *lower dunnet shale*. Strata 400–600 ft., sandstone, blaes, lime ribs.

Barracks shale. Very variable, sometimes 8 ft., and yielding 22 gals., but generally thinner and poorer.

Burdiehouse limestone. A well recognised position. Sometimes 64 ft. quarried. Strata 600 ft., blaes and thick sandstones.

Pumpherston shales, 5 of them, with about 12 ft. of blaes between each pair, respectively 8, 5, 6, 7, and 4 ft. thick, 16–20 gals., 50–70 lbs.

The lower division of the calciferous sandstone varies from a hundred to several thousand feet in thickness. Sandstones, non-bituminous shales, cement stones, &c., fill up the space until the upper old red sandstone is reached. The Wardie shales (11 gals., 20 lbs.) of this lower division would not pay to work under present circumstances; but richer parts of it might be discovered.

The oil shale measures are very much troubled. They are contorted into great waves, sometimes even overlap, and the same seams come to the surface at many places. There are four great faults running E. or N.E. with displacement of 1000–1500 ft., and numerous small faults or branches to the large ones. There are dykes of igneous rock running through the measures for miles. There are numerous necks of igneous rock coming up through the other strata; and there are many great sheets of intrusive sill intercalated between the normal strata, sometimes 5 or 6 ft. thick for a long distance, but here and there thickening to a great depth; sometimes keeping the same position for a wide space, then suddenly going higher or lower. The intruded mass has often taken the position of a good shale, utterly destroying it, and occasionally retaining some of the products of distillation in calcite-lined cavities in the mass of the sill, as liquid petroleum, solid bitumen, or substance of intermediate consistency like vaseline. Certain sedimentary strata are charged with petroleum and brine. The surface of the country has been partially levelled down in later ages by glacier action, leaving hills with crag and tail where the neck of igneous rock came up.

The calciferous sandstone turns up in a broad band from the east to the west of Scotland, but only in this limited locality of the Lothians has there been the suitable circumstances for

the rapid deposit and preservation of the organic material that gives value to the shale. This has been called *sapropel* on the Continent and *kerogen* in this country. It is composed partly of amorphous jelly and partly of microscopical algæ, spores, and other minute forms of life, that seem to have been deposited in a brackish lagoon where there was little circulation, so that on falling to the bottom they were enclosed in the mud and so preserved from decay. A layer of heavy sea water would lie on the bottom and protect the mud from the action of the lighter aerated fresh water on the surface. There have been great volcanoes in the neighbourhood active during the deposit of this formation which first may have stimulated the minute life by warmth and afterwards by eruption caused their sudden precipitation to the bottom and envelopment in the mud. Dust thrown out by volcanoes has formed extensive tuff strata throughout the district. Earthquake or poisonous gases may have caused the sudden death of the fish of the fish beds; and the many thin deposits of chemical limestone may have obtained the heat for the decomposition and precipitation of the bicarbonate from the neighbouring volcanoes.

The shales worked in France and Australia belong to the carboniferous or permo-carboniferous epoch. In New South Wales in the Blue Mountain region to the west of Sydney and Newcastle there is a large stretch of country in which oil shale is found. It is 250 miles long, north and south, and 90 miles at the broadest. It is a country of high mountains and inaccessible valleys, and has been explored only near the railways. At one place there is a seam with 1 ft. yielding 120 gallons, and $3\frac{1}{2}$ ft. 70 gallons. At another place $5\frac{1}{2}$ ft. of good shale with 4 in. coal below and 6 in. above, and the coal has to be removed, otherwise the condensers are choked up and the paraffin rendered impossible to refine to whiteness. There are seams of 6 ft. averaging 40 gallons, others 2 ft. averaging 85, and so on. Sometimes the shale is like cannel coal. Vast deposits still unworked are found in Canada in the upper old red sandstone. The Kimmeridge shale of England belongs to the Upper Jurassic. It is sulphury, but its distillation is being attempted in Norfolk Oil shale may be got through a great range of geological time. The United States of America has large fields of oil shale. It occurs in the Green River formation of early Tertiary Age in Colorado, Utah, and Nevada. There is 1900 square miles in Colorado, lying flat and undisturbed, and a larger area in Utah. The shale is light to dark brown, with light brown streak, smells of petroleum when broken; and weathers to light grey, and the better the shale the lighter in colour it gets. There are many seams of varying thickness and gallonage, and many have been tested. In one lot of 57 samples 18 yielded from 20 to 86 gallons per ton. The Green River formation has a maximum thickness of 2600 ft.; but only the middle part of 1500 ft. contains oil shale. Oil shale is found in Montana on the Big Blackfoot River, and in California in the Cholame Valley, and also in Kentucky.

Mining.—The working is much like coal, pillar and stall, and the pillars removed later. Coal-cutting machines are not used. More is done by blasting in shale mines than with coal, various explosives being used, but mostly gunpowder. Boring for the shots is now done at several places by electrical machinery, a hole being drilled in 5 minutes that takes 45 minutes by hand. The machine is heavy to move about, and has been discarded in some mines. Most of the haulage, pumping water, &c. is now generally done by electric power, raised by steam. Before sinking a mine or pit in a new neighbourhood it has to be well explored by boring as the seams vary much, and the vagaries of the intrusive sill cannot be foreseen. The workings vary from 0 to 1000 ft. in vertical depth, one pit reaching 1600 ft. A seam is often richer towards the outcrop and poorer as it increases in depth, but not always. There is a fan draught as in coal pits. The ventilation has to be good to sweep away the smoke of the shot-firing. Fire damp gives little trouble so that naked lights are in general use. A considerable proportion of the shale is got by mining from the outcrop, and then the water pumping is a serious item. A mine may have to pump 1500 gallons a minute in the wet season.

The manufacture is carried out in two divisions: I. the crude works, and II. the refinery.

I. *The crude oil works* consists of shale-breaking machines, retorts, condensers, receivers, scrubbing towers to take ammonia and light naphtha from the permanent gases of the distillation, a tower oil still and ammonia house. The crude works are situated in the middle of the shale field so that much of the shale is tipped into the breaking machine direct from the miners' hutches. It is expensive to convey shale far underground, and so mines or pits arc put down all over the field and the shale brought in railway waggons to be emptied by hydraulic machinery into the breaking machine. If shale lies 5 miles or more from the refinery a crude works is put up there and the crude oil sent to the refinery by rail in tank waggons.

The breaking machines consist of two strong-toothed cylinders between which the shale is broken into pieces about 4–6 in. square. One machine with cylinders 3 ft. diameter and $4\frac{1}{2}$ ft. long puts through over 500 tons in a day of 8 hours. The cylinders are of cast iron $3\frac{1}{4}$ in. thick with malleable steel teeth $2\frac{1}{8}$ in. diameter and projecting $4\frac{1}{2}$ in. outside the cylinder. The teeth of the one cylinder fall between the teeth of the other, and the clearance is self-adjusting 0–1 in.

Retorting.—The broken shale falls into hutches on rails holding about 18 cwt., to be taken by endless rope up an incline to the top of the benches and emptied directly into the retort hoppers. The retort hoppers are so large that filled by day there is sufficient supply for all night. After distillation and passing down through the retort the spent shale falls into a hopper below, which is emptied at intervals, by day and night into iron hutches to be convcyed by endless rope or chain to the top of thc spent shale bing.

Retorts now are all vertical and are arranged in two rows in benches of 44–66 retorts. The

distillation is upwards, and along the top of the retorts on each side there is fixed the main to carry off the products of distillation. The exit from retort to main is 7 in. diameter and the main itself 30 in.

The first retort used by J. Young in 1850 was an imitation of the horizontal iron gas-retort of the time, but worked at as low a temperature as possible. Young soon adopted a vertical retort, but other works continued to

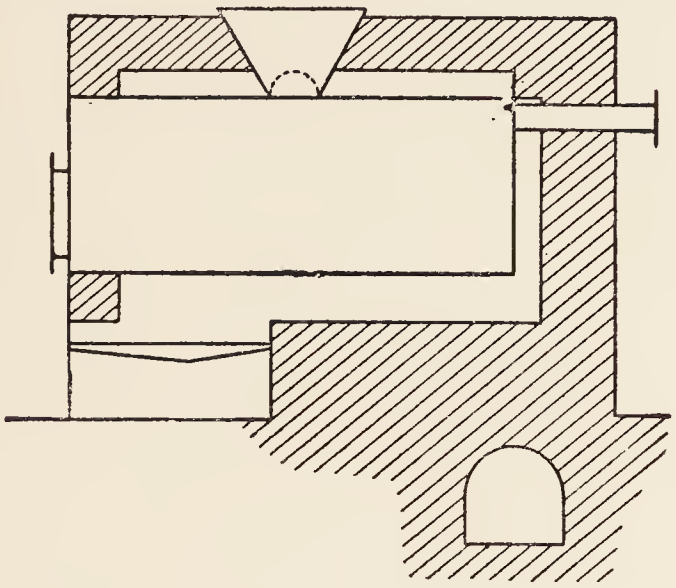


Fig. 1.

use the horizontal type with improved arrangements until 1880 (Fig. 1).

The old vertical retort (Fig. 2), a cylinder about 1½ ft. in diameter and 10 ft. long, had a bell-hopper above for charging, and a water-lute below through which the spent shale was raked. It was charged at intervals of an hour, and a corresponding quantity of spent shales was withdrawn half an hour after the charging. Vertical retorts, improved in form and setting, oval in section, and lengthened to 15 ft., were

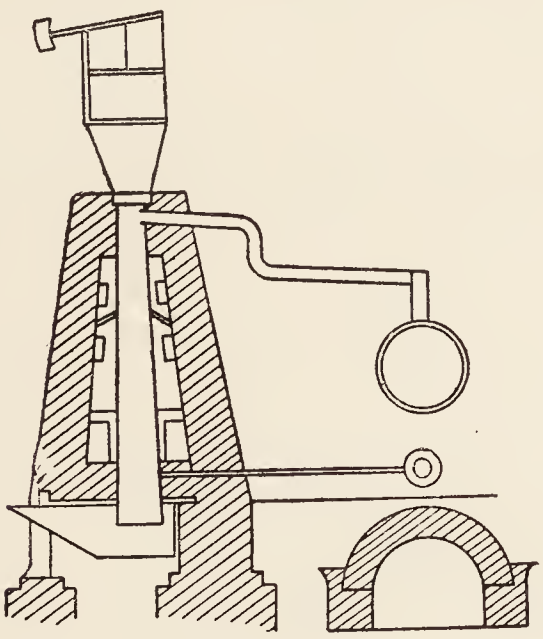


Fig. 2.

in use in some works until after 1880. About 1860 steam had been introduced into the bottom of the retort. It moderated and transfused the heat, and swept the oil vapours rapidly out of the hot region, and the crude oil was improved in quantity and quality. These retorts were fired by coal, and the coal furnace heated three retorts on each side of it. They were often overheated, spoiling the oil and destroying the retort. Young recommended 600°–700°F., but old vertical retorts sometimes reached 1200°–1500°F. as measured by Siemens' water pyrometer. The result was thus dependent on the care of men.

Many forms of retorts were patented. W. Young in 1867 tried a retort with gas-jacket around the metal retort. It was not a success, but it proved that a great improvement in the quality of the crude oil could be effected by gentle heating. The spent shale of the early retorts contained about 12 p.c. carbon, and a large proportion of the nitrogen. W. Young in 1872 attempted to utilise the spent shale for fuel with a gas lute between the products of combustion of the spent shale and the products of distillation. It required too much care in its management. N. M. Henderson in 1873 patented an arrangement by which the spent shale was dropped into a furnace below and served as fuel for the next charge (Fig. 3). This was an intermittent working retort. It held 18 cwt. shale, and was emptied and recharged every 16 hours. Four retorts were in an oven over one furnace and one was dropped

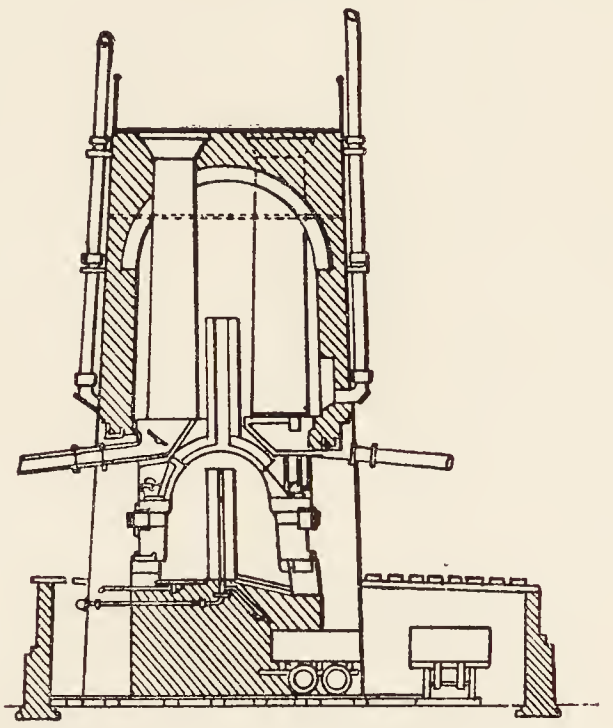


Fig. 3.

every 4 hours. The fuel bill was greatly reduced, and the power to overheat was taken from the men and a greatly improved crude oil was the result. This retort was widely adopted for some time. The distillation was downwards.

The modern type of retort was the invention of George Beilby and William Young, experimenting at first independently and afterwards in partnership. The Young and Beilby retort, 1881, Fig. 4, was a continuous working one, vertical, with upward distillation. The upper part made of cast iron, the lower part of fire-brick, with a great hopper, on the top of all, common to four retorts. They were heated by gas fuel in flues around the retorts giving a long passage to the burning gases. The shale took 18 hours to pass down through the retort. Steam introduced at the bottom was superheated at once by the hot spent shale. The temperature was not high enough for complete water gas, but the oxygen of the H_2O acted on the carbon of the spent shale to give CO and CO_2 in proportion according to the temperature, while the nascent hydrogen reacted on the

nitrogen of the shale to produce NH_3. The lower or brick part of the retort is thus an ammonia and gas producer, and is worked at a high temperature, as high as can be ventured without fusing the ash. The permanent gas produced was over 10,000 cu. ft. against 2000 or 3000 of the earlier retorts, and the ammonia was doubled. The oil distillation took place in the iron part of the retort at a much lower temperature. The gases from the brick part were passed up through the fresh shale in the iron part, supplying heat, cushioning the large molecules against decomposition and sweeping the products rapidly out of the heat. The presence of ammonia increases the yield of solid paraffin (Tervet). The exit for the products of distillation was from the top of the great hopper. The crude oil condenses on the cold shale at the top to be redistilled as the shale slips further down, and it was claimed that a distillation of the crude oil in refining was saved. For extra fuel gas required, a coal gas-producer retort was

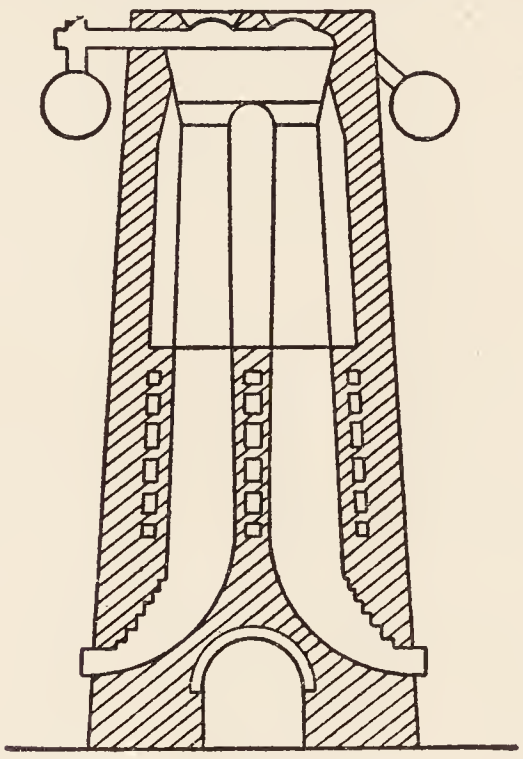


Fig. 4.

placed here and there in the bench among the retorts, and the ammonia recovered; but such coal retorts were soon disused.

All the present retorts are of the Young and Beilby type. The form used by Young's company is very like the old Young and Beilby (Young and Fyfe, No. 13665, 1897; and No. 15238, 1899).

The retorts known by the names of Fyfe, Bryson, Crichton, and Henderson have this in common that they have a mechanical arrangement at the bottom of the retort, supporting the whole column of shale and spent shale, going constantly and regulating the amount put through. Bryson's, for instance, is a table with a revolving rake, Henderson's is two toothed rollers slowly revolving.

Henderson lengthened the retorts boldly and used Wilson's gas producer for supplementary fuel; but the larger size now used is so economical of heat that a 22-gallon shale requires no extra fuel of any kind, and has often excess of permanent gas so that after heating the retorts some is left to help in raising steam. The Henderson retort (Fig. 5) is now made in the metal part 14 ft. long, in the brick part 20 ft., and the total height to top of hopper is 63 ft. The section is oblong, 2 ft. 9 in. by 1 ft. 3 in. at the top of the metal part, and 4 ft. 8 in. by 1 ft. 10 in. at the bottom of the brick part. Each retort puts through $4\frac{1}{2}$ tons in 24 hours, and the shale is in the retort for 27 hours (Patents No. 6726, 1889; and No. 26647, 1901).

In the Bryson retort (patented by Bryson, Jones, and Fraser, No. 8371, 1894; No. 7113, 1895; and No. 4289, 1897) (Fig. 6) the section is circular, This form gives strength and longevity and it can stand a higher temperature of working than other forms. The iron part is 15 ft. and the brick part 17 ft. 10 in. long; the diameter 2 ft. at the top of metal, 2 ft. 4 in. at bottom of metal, and 3 ft. at bottom of brick part. The bottom hoppers of the retorts of the two rows in a bench converge so that a single line of rails under the centre of the bench

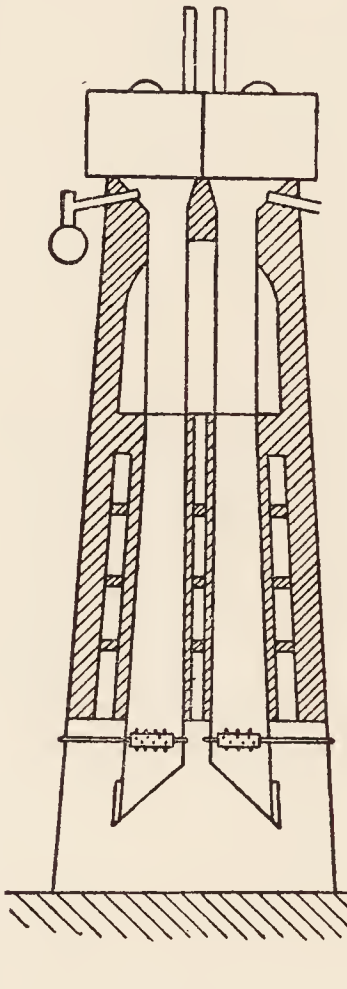


Fig. 5.

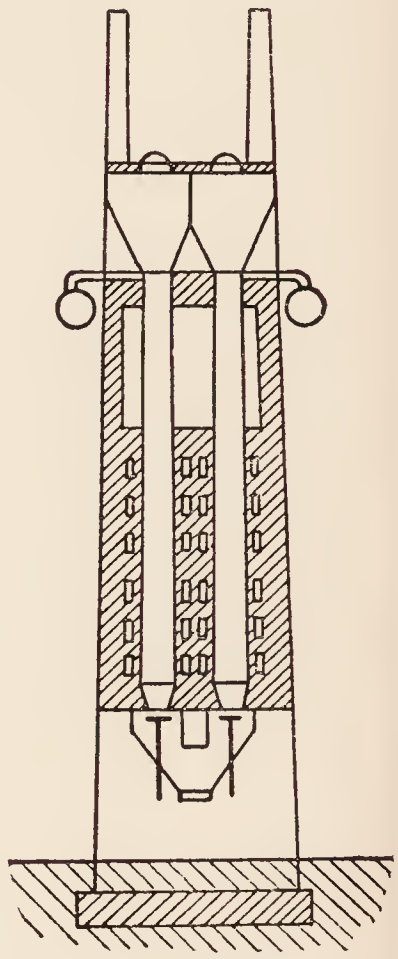


Fig. 6.

receives the spent shale from both sides into a hutch, and reduces labour to a minimum.

These large modern retorts are never stopped for cleaning or any other purpose. The yield of ammonia is triple that of any retort previous to Young and Beilby's.

The temperatures of the flues around the Henderson retort, determined with the Féry radiation pyrometer, are, near the bottom of the brick part, 1000°C. (1832°F.), near the top of the brick part, 850°C. (1562°F.), and in the oven of the metal part, 670°C. (1238°F.). The temperatures used in the Bryson are much higher.

The products of retorting are crude oil, fuel gas, ammonia water, and spent shale. The great hills of spent shale are a conspicuous feature in the shale districts. The spent shale of the retorts previous to Henderson's 1873 patent contained 10–12 p.c. carbon and a large proportion of the sulphur. It gave trouble in the great heaps or bings by igniting spontaneously

and burning quietly, giving off volumes of fumes containing SO_2 and H_2S. The well-exhausted spent shale of the present day is free from the nuisance. The original shale contains 1½ p.c. sulphur.

The crude oil of the old vertical retorts was dark and tarry, sp.gr. 0·880–0·895. Henderson's 1873 retort produced a crude oil, sp.gr. 0·865–0·870, which yielded 2½ p.c. more total products, all of improved quality, and contained 2½ p.c. more solid paraffin. The Young and Beilby retort gave a slightly increased quantity of crude oil and of solid paraffin. The Bryson retorts are worked at a high temperature to produce a crude oil of 0·880 sp.gr. rich in paraffin but somewhat difficult to refine. The present Henderson retorts are worked at a mild temperature to give a crude oil of sp.gr. 0·868 and of good quality.

Retort condensers.—The vapours are led first through a tubular tower in the pipes of which the water for the steam boilers is heated; then through condensers. Many forms have been tried, but the universal arrangement now is great benches of 4-in. pipes, cooled by the atmosphere, and sometimes having a little water sprinkled over them. The pipes, 27 or 36 ft. high, are arranged vertically and fixed below in two rows into chests, two dozen pipes for the descending gases and the same number for the ascending, with arched connections at the top. There is about 100 lineal feet of this piping, or 100 cub. ft. of surface, for each ton of shale put through per day per retort. The water and oil condense separate from each other at once in a box called a separator and are run into their several receiving tanks. The gases pass from the condensers through scrubbing towers; one or two in series of water towers to catch the ammonia, and one or two of oil towers (oil sp.gr. 0·850) to catch the last of the condensable spirit. The gas is then caught by a fan which sucks the gases through the towers and condensers and pushes it forward to the retort flues where it is burned. The fan causes a suction equal to 6 in. of water, and this vacuum passes back to the retort, being equal to ½–2 in. water at the retort exit. After burning in the flues of the retorts the products of combustion are passed off into the atmosphere by little chimneys at the top of the retorts, or are gathered into a common flue and taken to a tall chimney stalk. J. J. Coleman had a method of extracting gasolene from the permanent gases by cold and pressure. It was expensive, and has not been used for many years. The filling for the scrubbing towers now used is very various.

The ammonia water distillation is carried out in column-stills (Fig. 7), generally of circular section, and filled with a dozen or more trays. The feed water, after being heated in an exchanger by the spent ammonia water, travels down the column from tray to tray, while steam introduced at the bottom bubbles through each tray and liberates the free ammonia. Milk of lime is pumped into one of the trays near the bottom to release the fixed ammonia. The ammonia gases are led from the top of the still down to a 'cracker box' or saturator containing dilute sulphuric acid, and into which oil of vitriol is constantly run in a thin stream, and the ammonia is distributed from perforated lead pipes laid near the bottom. The bottom is sloped and the solid ammonium sulphate formed is swept into a well from which it is lifted by a steam injector and thrown into a conveying tub above, and the liquor lifted drains back into the cracker box, while the salt, after draining, is emptied into a bin. Here it drains or dries for a week before being ready for bagging for the market. The salt is now often centrifugaled direct from the saturator when it is ready for the market at once.

Acid water recovered from the acid tar of the oil refinery is saturated with ammonia in a somewhat similar manner. The saturation has to be complete, so as to separate the impurities. The excess of ammonia which escapes is caught in a vessel at a higher level containing the next charge of acid. The basic tar rises to the surface carrying with it the arsenic and the iron oxide, and is used as fuel. The solution of ammonium sulphate requires to be evaporated down. The oil of vitriol in the cracker box, previously described, requires diluting, and this solution is used. Any solution left is evaporated down in a vacuum pan something like those used for sugar, and the salt is sent into a centrifugal machine to dry it. Before evaporating down, the solution gets slightly acidified, otherwise ammonia is lost and the salt does not crystallise properly.

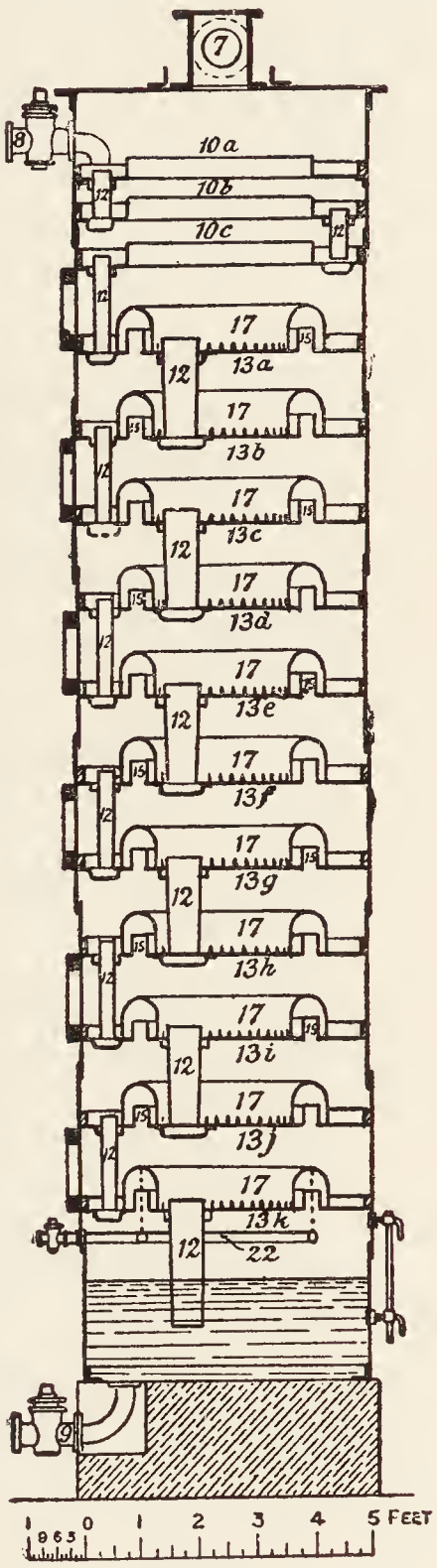


FIG. 7.

The steam from the cracker boxes containing CO_2 and some H_2S is passed into the shale retorts along with steam from the steam boilers.

The spent water has a strong smell and dark colour. It is pumped up and distributed over the hot spent shale on the bing where some is evaporated and the rest is filtered and passes off at the bottom of the heap, clear, colourless, and almost free from smell. Other dirty water is clarified in the same way.

The low temperature distillation of brown coal or lignite for oil products requires a very special quality: the most is useless for this purpose. Much money has been lost distilling unsuitable

material. To distinguish good from bad from this point of view requires expert advice or chemical examination. Brown coal exists in great quantities in Canada, Australia, and the United States, and is worth investigating from this point of view. Germany has very extensive fields of brown coal, but only in two places is suitable material found, viz. at Halle in Saxony, and near Darmstadt.

There are a dozen brown coal distillation works in the Halle region. Over a million tons are distilled anually from 1300 retorts, producing 60,000 tons of crude oil, sp.gr. 0·850–0·910, and 7000 tons of paraffin wax. The burning oil, sp.gr. 0·825–0·830, requires special burners, and much is now used for internal combustion engines. The heavier oils, called yellow oil, red oil, and paraffin oil are used for internal com-

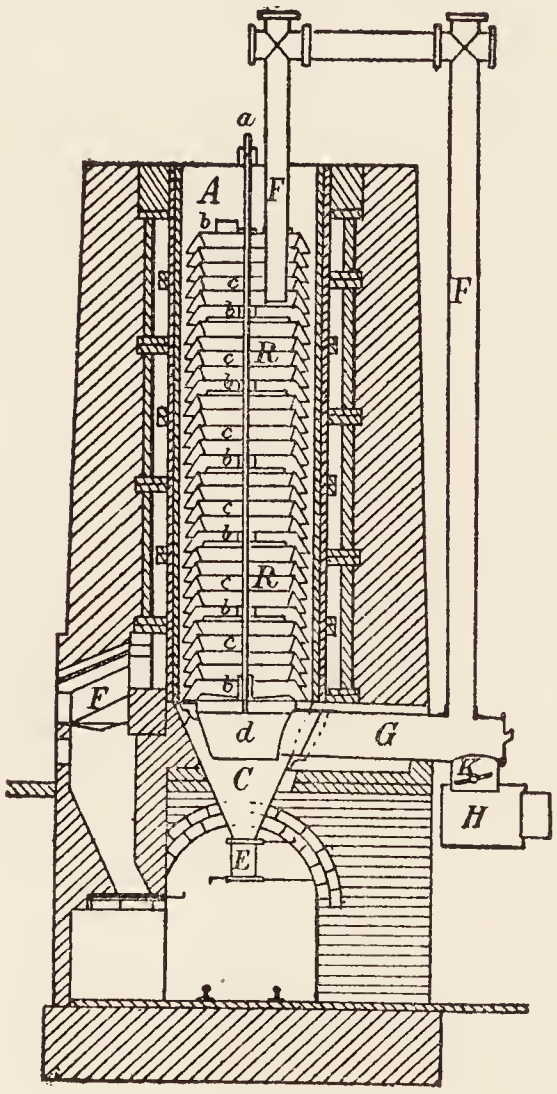


FIG. 8.

bustion in Diesel engines, and for gas making, gas enriching, and liquid fuel, and not much for lubricating. The retorts used (Fig. 8) are vertical and of circular section. The outer wall is of firebrick surrounded by heating flues. The inner wall is formed of iron rings built together, louvre fashion, with openings between them. The shale moves down continuously in the space between the iron rings and the brick wall, and the central tube formed by the rings receives and carries off towards the condensers the products of distillation. The retorts vary in size. A cylinder 16½ ft. high and 6½ ft. wide puts through 20 tons of brown coal in 24 hours. The heating is done by the retort gas, or helped with lignite. At Messel the material is unique: the bitumen is in chemical combination with mineral matter and cannot be extracted with solvents. It has a high percentage of moisture like ordinary brown coal. A special retort is used which is of interest, as the moisture of the coal is used to supply steam for the distillation; and the method might be adopted elsewhere and perhaps even for bituminous peat. A vertical section of the retort is shown in Fig. 8, *a*. It is of a type somewhat similar to Scottish retorts. (D. R. P. 200, 602, May 23, 1906). It works continuously. The top two-thirds is of iron; the bottom third of brick, and this is a gas producer, and from it the coal ash is dropped into a hutch below. In the top part of the retort the coal is dried, and the steam resulting drawn off by an electrically driven fan; a part is returned into the retort half-way down the metal, and part, caught by another fan, is passed into the bottom of the gas-producer, where, superheated, it acts on the carbon and nitrogen to make water-gas and ammonia. The oil distils off at the middle of the retort and is led away from near the bottom of the iron part to the condensers. The heating flues around the retort are much more spacious than in shale retorts, and are divided by partitions into compartments; and from one compartment to the one above it, there is communication by a comparatively small passage. The result is that there is a surging circulation of the products of combustion in each compartment, keeping it at the required temperature, and only a quantity passes off to the chimney in proportion to the draught. The oil vapours from the retort are passed through condensers and scrubbers and the permanent gas is returned to be burned in the retort flues. There is more gas than is required and the surplus goes to the power station.

In France shale is distilled in three oil works, one at Autun (Saône-et-Loire) and two at Bruxière-les-Mines (Allier). 160 retorts are in operation, distilling 150,000 tons yearly, and producing 2,440,000 gallons crude oil. The newer retorts are of the Young and Beilby type. The yield of crude oil is about 17 gallons to the ton, sp.gr. 0·912, and contains less than 3 p.c. paraffin. The crude oil is difficult to refine, and the burning oil is rather poor in quality. The gas oil is in large proportion. The lubricating oil, however, is of very good quality. The ammonium sulphate varies from 13 to 23 lbs. per ton. Two companies turn out coal from the shale mines and the other one works torbanite to sell to the gasworks; none work shale alone.

In Australia little shale is being distilled at the present time; but a few years ago two large companies erected retorts and refineries in New South Wales, about 130 miles from Sydney. At present, 1918, one is temporarily stopped but the other continues, helped by a Government subsidy. From the mines are to be got shale, torbanite, and common coal. The mining is mostly done on the long-wall system, and no explosives used. The shale expands whenever the pressure is removed from it, and when undermined by the pick it soon falls down in pieces.

II. *The refinery* operations are distillations with fractionation into the several products; treatments with oil of vitriol and caustic soda; the recovery of the chemicals and the preparation of the tars for liquid fuel; cooling and refrigeration of the heavy oil, and filter-pressing to separate the liquid from the solid; and the sweating of the paraffin for its refining. Associated with the refinery is the despatch

department with the oil-filling into barrels and railway tanks.

The stills are built in great benches with rows of high tanks built on roundels of circular brickwork, from which the oil flows by gravitation into the stills, and rows of tanks at a low level to receive the distillates. The system used by all the works is Henderson's continuous process (*see* Fig. 9) or a modification of it. There are cylindrical boiler-stills lying alongside each other, or sometimes waggon-shaped stills for the crude oil, connected together into a series through which the oil flows continuously, distilling off a fraction from each still, and venting finally into one of a group of residue stills. By means of a pipe within a pipe the oil flowing from the charging tank is heated by the vapours distilling from the second boiler of the series, and is landed hot inside the front of the first still. It travels from the front to back, distilling off the lightest oil, which is condensed in a worm tank condenser. The oil not distilled is taken by a pipe and landed inside the front of the second still of the series, and it travels from front to back distilling off a second and heavier fraction; and on it goes through other boiler stills it may be, until at last the residue oil is passed into a still with pot-shaped cast-iron bottom. The residue still before being connected has a fire applied and steam passed through the still until all the air is blown out, so as to prevent explosion. Then the oil from the last boiler still is run in for some hours until the residue still is sufficiently loaded when the oil is shut off from this still and turned into another one. The disconnected still in then distilled to dryness and coked. There are safety valves on the residue stills in case the condenser should choke up with solid paraffin. At first two long troughs were suspended near the bottom of the cylindrical boiler stills to catch any coke or dirt in circulation; but these have been long disused. In all the distillations steam more or less superheated is passed into the distilling oil as it lowers the boiling-point and helps to carry the vapours over into the condensers. The first or crude oil distillation is meant to be to some extent a destructive one. If the chemical treatments with acid and soda were given direct to the crude oil the loss would be great; or if too much steam is used the oil distils over unchanged with the same result. So the steam is limited for the first distillation and also near the end of the second; but for the third distillation of the heavy or lubricating oil excess of steam is used: it helps to keep the viscosity of the oil high. In the lubricating oil distillation also dry caustic soda is put into the still, 2–5 lbs. per 100 gallons of oil. The condensers are coils of pipes laid in square iron tanks, carrying the vapours downwards, and cold water is passed into the bottom of the tank outside the pipes and overflows hot at the top, and the flow of water is regulated to suit the volatility and setting-point of the distillate. The condensed oil coming from the bottom of the condenser is passed through a U-bend of 8 in. depth on its way to the receiver, but before the bend a pipe rises vertically to take away the gases to prevent them being disagreeable or dangerous at the worm end. The gases used to pass into the atmosphere some yards up, now they are all caught and used for fuel or illumination. They are very rich and, from the second distillation especially, very pure. At coking of the residue stills and approaching the coking, torrents of permanent gas containing some light spirit are given off. Each works had its own method of catching the gases. In Henderson's system the

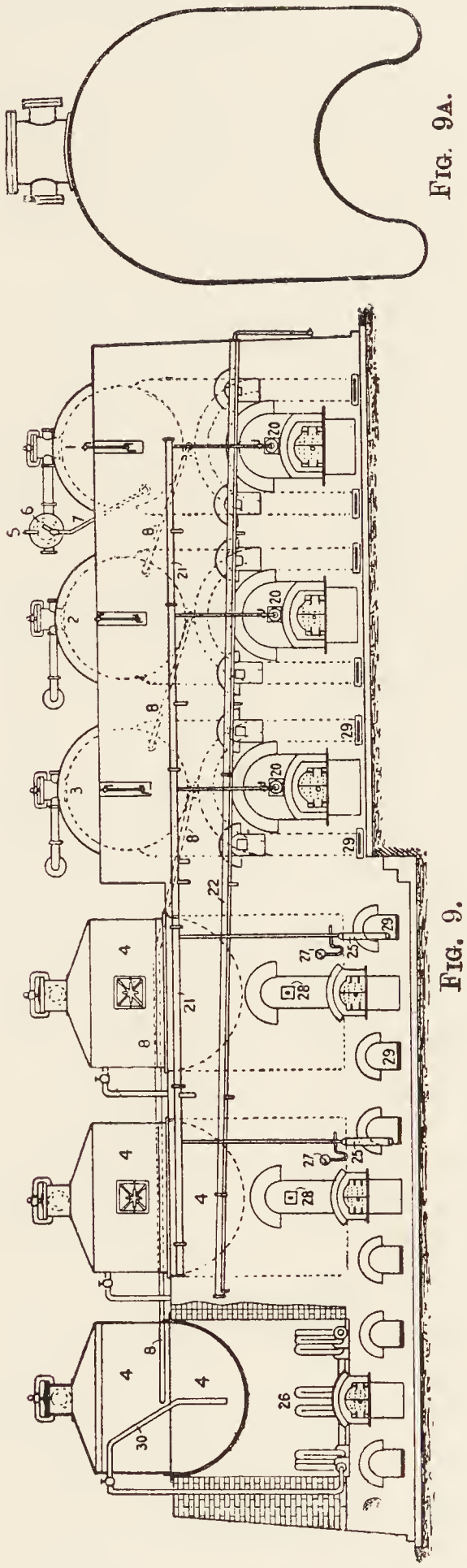


Fig. 9A.

Fig. 9.

gases are caught by a suction pump through a lute in a main common to a whole bench, the suction being automatically regulated so as not to suck air back through the bend of the oil exit.

In the first distillation many residue stills are required, in the later ones the distillation is mostly done in the boiler stills.

First distillation.—The crude oil is sometimes distilled from waggon-shaped boiler stills

of this section (Fig. 9A), but oftener horizontal cylinders 7 ft. diameter by 19 ft. to 9 ft. by 30 ft. are used, the charge being 2000–4000 gallons. The boiler stills are connected sometimes two in a series, sometimes three; or occasionally a central charging still supplies a boiler still, or even two, at each side. In all cases the tails run to residue stills. When two boilers are in a series, the distillate of the first is 0·760-0·770, of the second is 0·820–0·850, while the third in the series, the residue still runs from 0·850 or so when first connected to 0·930 or higher at the end of the distillation. At the end of the residue still distillation there comes over a yellow viscous product called still grease or chrysene which is used for grease making, or for liquid fuel.

For an output of 50,000 gallons a day 4 or 5 boiler stills are required for the crude oil distillation with about 22 residue stills of 2000 gallons capacity each. The residue stills are connected for 4–6 hours each before disconnecting to distil to dryness. The still coke is copious and valuable.

The distillate of the first boiler still is kept apart as *green naphtha*, the distillates of the others, boiler stills and residue stills, are generally run together as *green oil*.

Treatments.—The green naphtha gets 2 p.c. oil of vitriol and is stirred mechanically, the black tar settled and run off, and the oil is run off into another vessel where it gets stirred with about 1 p.c. of caustic soda solution of 1·3 sp.gr. The naphtha is then ready for another distillation with steam alone, and after that it is colourless, but generally gets another treatment with acid, ¼ p.c., and caustic soda and a finishing distillation, to improve the smell. Distillates are sometimes separated as light as 0·660, but the usual gravities are between 0·700 and 0·750, 0·700–0·720 being sold as motor spirit, and the higher gravities for solvents, &c.

The green oil, sp.gr. 0·855, gets a 2 p.c. treatment with oil of vitriol, the black tar settled and separated and the oil run into another vessel, where it gets 1 p.c. of caustic soda solution, and after settling and running off the tar, it is ready for another distillation. All the stirrings, except for the naphthas, are done by compressed air. The green oil is stirred with the chemicals in large vessels, 30,000–40,000 gallons capacity, cylinders on end with cupped bottom into the centre of which the air is pressed. In the later stirrings the vessels are sometimes horizontal cylinders with the air distributed along the whole length of the bottom. After the stirrings the vessels are closed tight and the air pressure put on the surface to send the oil up into the charging tanks for next distillation. Sometimes the oil is pumped up.

The second or green oil distillation.—For 50,000 gallons a day of crude oil, five boiler stills are required, two receiving the charge and the other three in series, and the tail to residue stills of which there may be ten or more.

1. The distillate of the two charging stills is about 0·800 sp.gr. It requires ¼ p.c. oil of vitriol and caustic soda, and a final distillation before the finishing treatment.

2. The second boiler in the series has sp.gr. about 0·815. It sometimes gets two treatments of ¼ p.c. oil of vitriol and caustic soda and two distillations before it is ready for the market, sometimes only one treatment and distillation.

3. The third boiler distillate is about 0·840, and after the paraffin is extracted is ready for market as gas oil or fuel oil of 0·850 sp.gr. Sometimes it is treated and distilled with finishing treatment for intermediate products.

4. The fourth boiler distillate and the distillate of the residue stills run together, give heavy oil containing paraffin, which, after separation of the solid paraffin as afterwards described, is *blue oil*. This gets 1 p.c. oil of vitriol and caustic soda, and is distilled again and fractionated into the various grades of lubricating oil, sp.grs. 0·865, 0·875, 0·885, and 0·895. The blue oil distillation is sometimes carried out at once in 5000 gallon pots-stills (*see* Fig. 10) with dry caustic soda and excess of steam, sometimes it gets a concentration by passing through two boiler stills and the residue distilled in the pot stills with caustic soda. The crude oil and green oil residue stills and often the lubricating oil stills are as shown in Fig. 11. Different works have somewhat different distilling arrangements and treatments, and even the same works is always changing somewhat to suit circumstances.

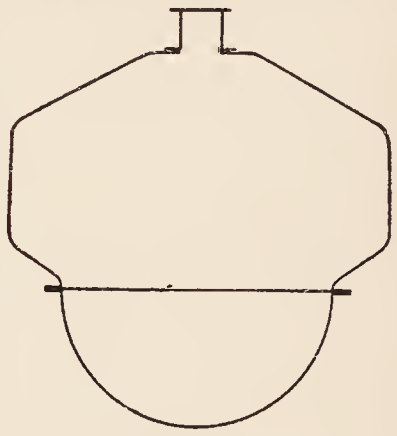


Fig. 10.

Finishing treatments.—Burning oil is treated with ½–1 p.c. oil of vitriol, and with weak caustic soda solution of about 1·04 sp.gr., and then with a little caustic soda solution of 1·33 sp.gr., and after settling is filtered through a filter press with paper instead of cloth. It is nearly water-white.

The heavy oils are treated with 2–4 p.c. oil of vitriol according to gravity, are settled all night, then finished with solution of sodium carbonate, as weak caustic darkens heavy oil, and after settling bright pumped to the filling tanks. It sometimes requires two or more days to settle the heaviest lubricating oils to brightness, and the following method has been tried for rapid clarifying. After the sodium carbonate tar is run off, open steam is blown in until boiling freely through the oil, then settled—and it settles rapidly at the high temperature—and the soda water is run off completely. Finally, air is blown through the hot oil until the oil is bright.

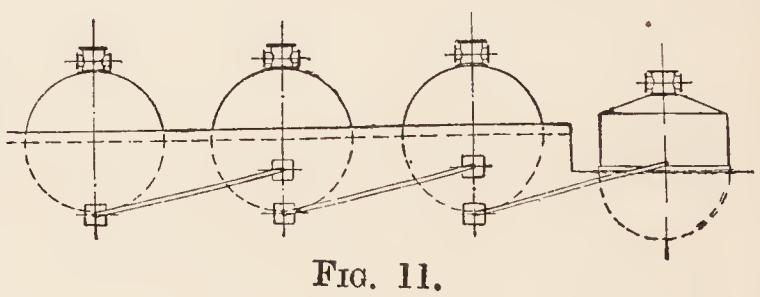


Fig. 11.

The soda tar of the finishing treatments is white.

The vitriol tar is washed with hot water stirring the mixture with air and settling. This is done twice. The water seizes the sulphuric acid, and sets free the tarry bases. These are

settled free from water, and burned under the boiler stills, &c., sprayed with superheated steam. The recovered acid is sent to the sulphate house to get saturated with ammonia as already described.

Separation of the solid paraffin.—The heavy oil containing paraffin from the second distillation is cooled and pressed twice; the first time to separate hard paraffin scale, and the second time with greater cooling to separate soft scale. One method is: The heavy oil containing solid paraffin is air-cooled in shallow tanks in covered sheds open to the wind, and in long cylinders with an inside stirring paddle. After this it is transferred to a cooler which is a tank divided into 6-in. wide spaces for the paraffin mass by 1-in. partitions containing circulation brine of calcium chloride from an ammonia freezing machine. The chilled part is constantly removed from the partition by a spring scraper. The mass lies in the cooler, in this first cooling for 6 hours, until chilled to 32°F. The filtered oil is subjected at once to a second cooling for 10–11 hours, until 14°F. and after filter-pressing the oil gets its sulphuric acid and caustic soda treatments and is distilled as described, and the lubricating oil fractions require no more cooling and pressing, except for the light intermediate oil fraction, where somehow any solid paraffin present accumulates. If after the first cooling and pressing to separate the hard paraffin the blue oil gets its treatments with chemicals then, after distillation, the various fractions of lubricating and intermediate oil have to be separately cooled from 12 to 24 hours and filter-pressed. The heavier viscous lubricating oils are difficult to manage in this way: they do not separate from the crystals of paraffin so readily in the filter and plate-presses, or in the sweating house. There is faster and more perfect separation when the chilling is carried out on the mixture of lighter and heavier oils before the final fractionating distillation. After being broken up by a mechanical stirrer the chilled masses are passed with considerable pressure through filter presses. The cakes of paraffin scale dropped from the filter-presses sometimes after melting up and recrystallising are sent direct to the sweating stoves without pressing in hydraulic plate presses. In other cases it is plate-pressed to separate the last of the oil.

Another method is: The mixture of heavy oil and paraffin is cooled in a tower by air current, then passed into a long vessel containing a stirrer where it is cooled by a cold-water jacket, afterwards passed into a cooler with stirrer where it is chilled by a jacket of the cold oil from the filter presses, then at last into a tube which may be vertical or horizontal, 17 in. diameter, with a scraper inside surrounded by a wider tube containing liquefied ammonia gas which is evaporating rapidly into the vacuum of a suction pump. The oil and paraffin mass thus gets the final refrigeration and passes under high pressure from a pump direct to the filter-presses. The separated oil on its way out chills the oil coming in as stated and passes to a tank to be worked up for lubricating oil. The solid paraffin falling from the filter presses is broken up and conveyed by archimedian screw into the plate-press house, where it is pressed in cloths in hydraulic presses, and the last of the oil expelled. After this the paraffin is ready for sweating.

This direct application of the cold is more economical of the refrigerating power, and although gradual cooling is applied as much as possible, yet the sudden chill at the end causes some paraffin to separate in the amorphous state, and more filter presses are required than with the more gradual cooling with the brine. The brine-cooled paraffin is more crystalline, and therefore the liquid separates from the solid much more readily in the filter presses.

Paraffin is refined by a sweating process. Cakes of paraffin made by cooling and crystallising the melted solid are heated up gradually, when the oil and soft paraffin sweat out carrying the colouring matters along with them. N. M. Henderson's method is the only one used in Scotland, and it is in general use over all the world (see Fig. 12). In a great oblong chamber are built nine tiers of iron trays, in two stacks, making 18 trays in all. They are 6 in. deep, with a wire gauze shelf fixed 2 in. above the bottom. The trays are first filled with water up to the level of the wire-gauze shelf from a pipe at the end, which has a cock to each tray; then 2 or 3

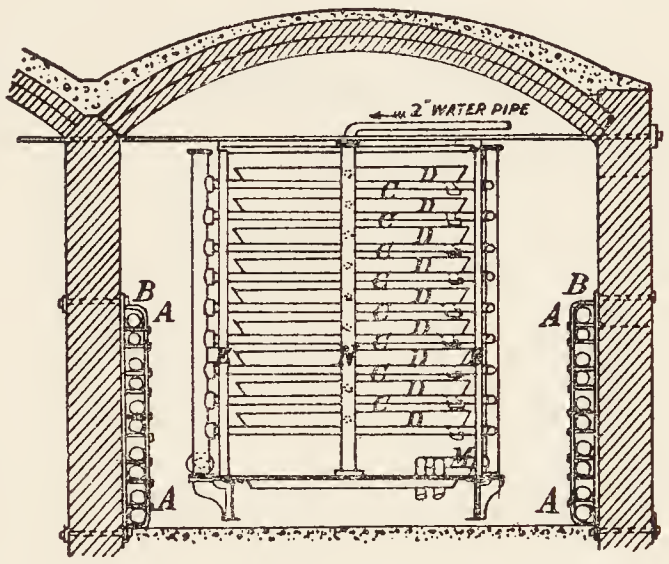


FIG. 12.

inches of liquid paraffin are run on the top of the water. The great end doors of the chamber are open, and large apertures in the roof so that cooling takes place by natural draught. Sometimes artificial wind from a fan such as is used for mines is applied. When the paraffin is cooled and solidified, the water is run off from below, leaving the great cakes lying on the gauze shelf. By turning a large screw the trays are slightly tilted to help the draining. The doors are shut, and spent steam from pumps and engines is turned into heating pipes ranged up the sides of the apartment, and the temperature gradually rises. The oil and softest paraffin gradually drain out from the hard crystals, and the sweatings are fractionated into receivers according to setting or solidifying point and colour. When sufficiently sweated, live steam is turned on to pipes which support and separate the trays, and the refined wax is melted and run out into its own tank. Semi-refined wax is got by one sweating, and a repetition of the sweating produces refined wax; sweating in itself being sufficient. But sometimes the refining is finished by melting the semi-refined wax, mixing 33 p.c. of spirit of sp.gr. 0·735, cooling into cakes and pressing them, folded in cloth, in hydraulic

Normal Paraffins C_NH_{2N+2}.

	Boiling-point.		Melting-point.		Sp.gr. of liquid.			State at ordinary temperature.
	°C.	°F.	°C.	°F.	°C.		°F.	
CH_4	163·9	(−263)	−186·1	(−303)	·415 at	−186·1	(−303)	Gas
C_2H_6	−83·9	(−119)	−172·2	(−278)	·446 ,,	0·0	(32)	,,
C_3H_8	−33·3	(−38)			·536 ,,	,,	,,	,,
C_4H_{10}	+1·1	(+34)	−135·0	(−211)	·600 ,,	,,	,,	,,
C_5H_{12}	36·1	(97)	−131·1	(−204)	·628 ,,	15·6	(60)	Liquid
C_6H_{14}	68·3	(155)	−93·9	(−137)	·661 ,,	,,	,,	,,
C_7H_{16}	98·4	(209)	−97·2	(−143)	·686 ,,	,,	,,	,,
C_8H_{18}	125·6	(258)	−56·1	(−69)	·705 ,,	,,	,,	,,
C_9H_{20}	150·1	(302)	−50·9	(−60)	·721 ,,	,,	,,	,,
$C_{10}H_{22}$	172·8	(343)	−31·1	(−24)	·733 ,,	,,	,,	,,
$C_{11}H_{24}$	193·9	(381)	−26·1	(−15)	·774 at m.p.			,,
$C_{12}H_{26}$	212·8	(415)	−12·2	(+10)	·773 ,,			,,
$C_{13}H_{28}$	234·0	(453)	−6·1	(21)	·775 ,,			,,
$C_{14}H_{30}$	252·3	(486)	+5·5	(42)	·775 ,,			,,
$C_{15}H_{32}$	270·6	(519)	10·0	(50)	·775 ,,			,,
$C_{16}H_{34}$	287·8	(550)	17·8	(64)	·775 ,,			Solid
$C_{17}H_{36}$	302·8	(577)	22·2	(72)	·776 ,,			,,
$C_{18}H_{38}$	317·3	(603)	27·8	(82)	·776 ,,			,,
$C_{19}H_{40}$	330·1	(626)	32·2	(90)	·777 ,,			,,
$C_{20}H_{42}$	205·0	(401 at 0·6 inch.)	36·7	(98)	·777 ,,			,,
$C_{21}H_{44}$	213·9	(417 ,,)	40·6	(105)	·778 ,,			,,
$C_{22}H_{46}$	224·5	(436 ,,)	44·5	(112)	·778 ,,			,,
$C_{23}H_{48}$	234·0	(453 ,,)	47·8	(118)	·778 ,,			,,
$C_{24}H_{50}$	242·8	(469 ,,)	51·1	(124)	·778 ,,			,,
$C_{27}H_{56}$	270·1	(518 ,,)	59·5	(139)	·779 ,,			,,
$C_{31}H_{64}$	302·3	(576 ,,)	68·3	(155)	·780 ,,			,,
$C_{32}H_{66}$	310·0	(590 ,,)	70·0	(158)	·781 ,,			,,
$C_{35}H_{72}$	331·1	(628 ,,)	75·0	(167)	·781 ,,			,,
$C_{50}H_{102}$	422/15m	(792)	93·0	(199)	·794 ,,			,,
$C_{60}H_{122}$			101·1	(214)				,,

Olefines C_NH_{2N}. Carbon 85·7 %. Hydrogen 14·3 %

	Boiling-point.		Specific gravity.		Melting-point.	
	°C.	°F.	°C.	°F.	°C.	°F.
C_2H_4	−102·8	(−153)				
C_3H_6	−180·0	(−292)				
C_4H_8	− 5·0	(+23)				
C_5H_{10}	+39·5	(103)				
C_6H_{12}	67·8	(154)				
C_7H_{14}	98·2	(208)	·706 at	15·6 (60)		
C_8H_{16}	123·9	(255)	·723 ,,	(60)		
C_9H_{18}	140·1	(284)				
$C_{10}H_{20}$	172·4	(342)				
$C_{11}H_{22}$	195·0	(383)	·790 at	0·0 (32)		
$C_{12}H_{24}$	96·1 at 0·6 inch	15·2 (205)	{·762 ,, ·795 ,,	15·6 (60) m.p. }	−31·1	(−24)
$C_{13}H_{26}$	232·8	(451)	·844 ,,	0·0 (32)		
$C_{14}H_{28}$	127·3 at 0·6 inch	15·2 (261)	{·775 ,, ·7936 ,,	15·6 (60) m.p. }	−12·4	(+10·4)
$C_{15}H_{30}$	203·3	(398)	·814			
$C_{16}H_{32}$	273·9 (525° F. [311 at 0·6 inch])		{·790 ,, ·7917 ,,	1·6 (60) m.p. }	+ 3·9	(39)
$C_{17}H_{34}$	160·1 (320° F. at 0·6 inch)		·804 ,,	0·0 (32)		
$C_{18}H_{36}$	178·9 (354° F ,,	,,)	{·801 ,, ·7910 ,,	15·6 (60) m.p. }	17·8	(64)
$C_{20}H_{40}$	395·1	(743)	·871 ,,	0·0 (32)		
$C_{27}H_{54}$					57·2	(135)
$C_{30}H_{60}$					62·2	(144)

SOME TYPICAL NAPTHENES C_NH_{2N}. CARBON 85·7 %. HYDROGEN 14·3 %.

	Boiling-point.		Specific gravity.		
	°C.	°F.	At 0 °C. (32°F.)	°C.	°F.
C_6H_{12}	70·01	(158)	·7598	·7334 at 10·0	(50·0)
C_7H_{14}	100·0	(212)	·7778	·7624 ,, 17·8	(64·0)
C_8H_{16}	119·5	(247)	·7714	·7582 ,, 17·0	(62·6)
C_9H_{18}	135·6	(276)	·7808	·7652 ,, 20·0	(68·0)
$C_{10}H_{20}$	161·2	(322)	·795	·783 ,, 15·0	(59·0)
$C_{11}H_{22}$	180·0	(356)		·7995 ,, 17·0	(62·6)
$C_{12}H_{24}$	196·7	(386)		·8055 ,, 13·9	(57·0)
$C_{13}H_{26}$	232·8	(451)	·8445		
$C_{14}H_{28}$	240·1	(464)	·8390	·8190 ,, 17·0	(62·6)
$C_{15}H_{30}$	246·1	(476)	·8294	·8262 ,, 20·0	(68·0)

plate presses. The expressed spirit carries away all colour. The smell of spirit is removed by steaming. Sweatings are themselves sweated at a low temperature to get low melting-point waxes.

N. M. Henderson has adopted another method of sweating (see Fig. 13). The plant is cheaper, easier to erect, and more economical of space, and it gives a more thorough separation of oil from paraffin and a larger yield of finished wax. A cylinder 7 in. diameter is fixed concentrically within another of 17 in. diameter. Both are of thin iron, 9 ft. long, and fixed vertically. The centre one is open to the air, both at top and bottom. The outer one has a bottom with outlet pipe and cock, and also a false bottom a few inches up. Around the inner cylinder there are three plies of wire gauze. Water is run into the cell up to the false bottom, and the cell then filled with melted paraffin. After cooling in the same manner as the tray stoves, the water below is run off, and suction is applied to the bottom of the cells by a steam injector on the exit pipe common to a row of cells. The doors are shut and steam put on pipes laid below, and the sweatings find their way through passages formed at once by the heat among the layers of gauze. It has been proposed to expedite the operations by taking the chilled cakes falling from the filter presses, breaking them up and transferring at once to the cells, where the oil is sucked away before the cold paraffin reaches the atmospheric temperatures. The oil is free from dissolved paraffin. This saves the time and expense of melting up and recrystallising.



FIG. 13.

A double stove of 18 trays takes a charge of about 16 tons. Into the same space 144 cells are placed to hold more than twice the amount of paraffin.

In every case the final process is stirring the melted paraffin with 1 or 2 p.c. char (got from the old method of cyanide making) for 15 minutes, then at once, without settling, pumping the mixture first through a cloth filter-press, and then through one mounted with filter paper. These catch the char, and the wax is ready to run into cakes for the market, or direct into the candle-house tub. Long contact between char and wax is to be avoided, for soon the melted wax begins to take up the colour again. The char retains a proportion of wax. This is recovered by a still like a Soxhlet apparatus on a large scale. If the paraffin is thoroughly washed out, the char, when retorted, is as good as at first; but ½ p.c. of paraffin left in spoils it.

Two of the refineries have candleworks. They supply some wax to other candlemakers, but they also buy much foreign wax to convert into candles besides the bulk of their own production.

Two of the refineries make oil of vitriol for their own use. All recover sulphuric acid from the vitriol tar and use it for making ammonium sulphate. They also recover a proportion of the soda they use.

There are rows of tanks to stock all grades of oil, especially vast tanks to store burning oil for winter use, and Admiralty fuel oil, and they are connected by pipes with taps in the filling houses to run the oils into barrels or railway tanks, or into drums, or tins for cases.

There are tradesmen's shops, wherever needed for mines or works, for smiths, fitters, joiners, plumbers, &c., and also saw-mills, steam-hammers, box-making machinery, and other necessaries and conveniences. About 10,000 men in all are employed.

Shale oils are a mixture of the paraffin and olefine series with a proportion of naphthenes and a little benzenes. Tables of Paraffins, Olefines, and Naphthenes are appended. The paraffin table gives the normal members only, as examples, although the others are present. The isomers of the members are often numerous, and their properties differ from the normal. Pentanes boil at 97°, 86°, and 50°F.; hexanes at 155°, 147°, 144°, 136°, and 114°F., and so on. The more complex the side chains the lower the boiling-point. In the cases where the normal member is solid the isomers are often liquid.

The history of retorting, with many figures, is given by Beilby (J. Soc. Chem. Ind. 1897, 876); and in the same journal, 1897, are described the more modern retorts (Henderson, 984; Crichton, 988; and Bryson, 990). Refining is described (J. Soc. Chem. Ind. 1889, 100) with continuous distillation, &c.; brown coal (1917, 167). The Geological Survey of Scotland

has published a Memoir, The Oil Shales of the Lothians, giving Geology, Mining, Chemistry, and Works processes. D. R. S.

PARAFFINIC ACID, $C_{23}H_{47}COOH$, was obtained by Pouchet (Bull. Soc. chim. [ii.] 23, 111) by oxidising solid paraffin with nitric acid; m.p. 45°–47°.

PARAGONITE *v.* Mica.

PARAGUAY TEA or **YERBA DE MATÉ**, commonly known as *Maté*, or *Jesuits'* or *St. Bartholomew's tea*, consists of the dried leaves and shoots of *Ilex paraguensis* (A. St. Hil.) (an evergreen related to the holly) and other small trees of the same genus, growing in the mountain woods (known as Yerboles) of Southern Brazil, Argentina, and Paraguay. It is also grown in plantations and is now used as a common beverage by over 30 million of the inhabitants of the South American republics, but has not yet gained favour in Europe, although its use is increasing, especially in France and to some extent in Great Britain, owing to the shortage of ordinary tea during the Great War.

The trees are usually about 15 feet high, but occasionally attain a height of over 30 feet. The leaves are from 4 to 6 inches long, lanceolate, with finely serrated margins, and slightly obtuse apex. The midrib and its branches (the so-called 'veins' or 'nerves') are very prominent on the under side of the leaf. As in ordinary tea, the 'veins' meet before reaching the margin, and the stomata, which are nearly circular, are very numerous.

In the preparation of maté, whole branches, together with the twigs and leaves, are cut down, dried and roasted on iron gratings over a wood fire until the proper flavour is developed, then beaten with sticks and the fragments of leaves and twigs roughly ground to a very coarse powder to form the *Yerba de Palos* of the Spaniards or *Caa-Guaza*. Other and superior grades known on the South American markets are *Caa-Cuys*, derived from the young leaf-buds, and *Caa-Miri*, which consists of the unroasted leaves freed from their tough fibrous veins and midribs.

The infusion is made by pouring boiling water directly into the cup containing a quantity of maté with a little sugar and sometimes lemon-juice, and is imbibed while very hot through a *bombilla* or tube perforated at the bottom or provided with wire gauze to prevent the passage of solid particles of the tea.

It is said to have valuable restorative qualities after violent or prolonged physical exercise, due no doubt in part to the presence of caffeine or theine which, however, is present in smaller proportion than in ordinary tea (*q.v.*), but its effect is narcotic rather than stimulative. It also possesses mildly aperient and diuretic properties.

The amount of caffeine found in maté by different observers varies greatly, but trustworthy analyses do not show much more than 1 p.c. The tannin is peculiar in character, as it does not precipitate potassio-tartrate of antimony nor tan leather. Analysis of Paraguay tea yielded the following results: water, 9·00; water extract, 33·10; ash in water extract, 3·8; alkaloids, 2·1; tannin, 9·79; total ash, 6·62; soluble ash, 2·26; silica, &c., 1·44; alkalinity of ash (as K_2O), 0·69; crude fibre, 15·45; ether extract, 9·8; volatile extract, 2·05; nitrogen, 2·17; resins, 9·1 p.c. (Hennings, Ber. Deut. Pharm. Ges. 1920, 30, 22). J. C.

PARAHOPEITE *v.* Hopeite.

PARALACTIC ACID *v.* Lactic Acid.

PARALDEHYDE *v.* Aldehyde.

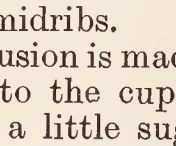
PARAMOL (*o* - amino - *m* - hydroxylbenzyl alcohol), $C_6H_3(OH)(CH_2OH)NH_2$, is a photographic developer, the action of which is intermediate between the developers of the phenol class and the amidophenol class (Eichengrün, Zeitsch. angew. Chem. 1901, 14, 1070). It is soluble in 12 times its weight of water, gives a bluish negative, and can be used for negatives, positives, and papers (Jahr, Brit. J. Photogr. 1902, 49, 32).

PARANEPHRIN *v.* Synthetic Drugs.

PARAPHENYLENE BLUE. This dye comes into commerce in three shades, which are designated respectively G, R, and B. They belong to a class of dyes obtained (according to Eng. Pat. 10134 of 1886) by heating paraphenylenediamine (or its homologues) with certain aminoazo- compounds—*e.g.* aminoazobenzene.

Paraphenylene blue R dissolves easily in water with a reddish-blue colour. Hydrochloric acid produces no change in the aqueous solution; but sodium hydroxide completely precipitates the dye in the form of a dark-violet precipitate. Tannic acid, in presence of sodium acetate, yields a blue precipitate, and the liquid is rendered colourless. The boiling aqueous solution yields a black precipitate with potassium dichromate. The reactions shown by the other shades are similar. On wool, paraphenylene blue dyes direct in presence of a small quantity of acid. On cotton it is fixed by means of tannin and tartar emetic. The shades obtained resemble those produced by methylene blue. When chromed after dyeing the shades become considerably darker (J. Soc. Chem. Ind. 7, 561).

PARATOPHAN. Methylphenylquinoline carbonic acid.

PARAXANTHINE, 1 : 7-*dimethyl*-2 ; 6-*dioxy*-*purine*  , was discovered by Thudichum (Ann. Chem. Med. 1879, 1, 163; Compt. rend. 1888, 106, 1805), and independently by Salomon (Ber. 1883, 16, 195) in human urine, of which it is a normal constituent, and occurs to the extent of 1·3 grm. per 10,000 litres (Salomon, Virchow's Annalen, 1891, 125, 554; Salomon and Krüger, Zeitsch. physiol. Chem. 1898, 24, 364); and it is found together with other methylxanthines in the urine of dogs and rabbits that have been fed with caffeine (Krüger, Ber. 1899, 32, 2818, 3336).

Paraxanthine can be prepared synthetically from theobromine (3 : 7-dimethylxanthine) by the following series of reactions: theobromine is converted by the action of phosphoryl chloride into 2 : 6-dichloro-7-methylpurine; this on treatment with aqueous alkali and subsequent methylation yields 2-chloro-6-oxy-1 : 7-dimethylpurine, which is converted into paraxanthine by heating with hydrochloric acid (sp.gr. 1·19) at 125°–130° (Fischer, Ber. 1897, 30, 2400). Paraxanthine can also be prepared by reducing with hydrogen iodide and phosphonium iodide 8-chloroparaxanthine obtained from 1 : 7-di-

methyluric acid by the action of phosphoryl chloride at 135°–140° (Fischer and Clemm, Ber. 1898, 31, 2622); by the action of boiling water on 8-chloro-3-chloromethylparaxanthine obtained by heating caffeine with phosphoryl chloride and phosphorus pentachloride at 158°–162° (Fischer and Ach, *ibid.* 1906, 39, 423); or by the action of nitrous acid on 1 : 7 dimethylguanine (Traube and Dudley, Ber. 1913, 46, 3839).

Paraxanthine crystallises in six-sided monoclinic plates, m.p. 298°–299° (corr.); in some preparations the crystals become cloudy or whitish at 110°, owing to loss of water of crystallisation, whilst others, isomorphous with them, remain bright (Salomon, *ibid.* 1883, 16, 195; Chem. Zentr. 1884, 490; Zeitsch. physiol. Chem. 1890, 15, 319). Paraxanthine is insoluble in alcohol or ether, dissolves in hydrochloric or nitric acid, or in ammonia; it is sparingly soluble in cold, more readily so in hot, water; at 40·1° 1000 c.c. of water or 1000 c.c N/10 hydrochloric acid dissolves 1·06 and 1·17 grm. of paraxanthine respectively; the aqueous solution is neutral, and the basic dissociation constant is $3 \cdot 29 \times 10^{-14}$ (Wood, Chem. Soc. Trans. 1906, 89, 1842).

In its physiological action on frogs paraxanthine acts similarly to xanthine, theobromine, or caffeine, affecting the central nervous system and the muscles, producing first creeping movements, then the disappearance of all spontaneous activity and complete abolition of reflexes; the lethal dose is 0·15–0·2 per 1000 of the body weight. On mice the drug produces paresis of the hinder extremities, increase of reflex activity producing tetanus, the lethal dose is 2–4 times as large as for frogs (Salomon, Zeitsch. physiol. Chem. 1889, 13, 187). Paraxanthine acts as a diuretic when administered to rabbits (Ach, Chem. Zentr. 1900, ii. 688), and is excreted partly unchanged and partly as 1-methylxanthine (Krüger and Schmidt, Ber. 1899, 32, 2677); it produces no toxic effects, and there is so little conversion into urea that it is probably not intermediary in the conversion of uric acid into urea (Lewis, J. Biol. Chem. 1915, 23, 281). It is of therapeutic value (Funk, J. Physiol. Chem. 45, 489).

Salts. (1) *With bases: sodium salt*

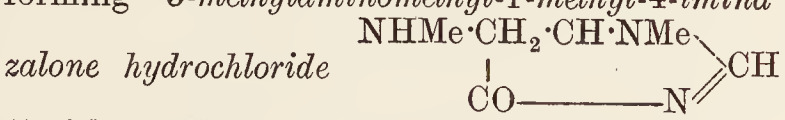
$$C_7H_7O_2N_4Na,4H_2O$$

sparingly soluble crystalline compound (Salomon, Ber. 1883, 16, 195; Fischer, Ber. 1897, 30, 2408). (2) *With acids:* the *hydrochloride*

$$C_7H_8O_2N_4 \cdot HCl,H_2O$$

forms rhombic plates, dissociates in aqueous solution and loses HCl and H_2O at 100° (Pommerehne, Arch. Pharm. 1898, 236, 105); the *hydrobromide* $C_7H_8O_2N_4,HBr,H_2O$ (Schwabe, *ibid.* 1907, 245, 398; the *picrate* forms a yellow crystalline precipitate, decomposing in aqueous solution; the *nitrate* is unstable. (3) *Double salts:* with *mercuric chloride*, colourless prisms, melting with partial decomposition; the *aurichloride* $C_7H_8O_2N_4,HAuCl_4,\frac{1}{2}H_2O$, orange-yellow needles, m.p. 227°–228°; the platinichloride $(C_7H_8O_2N_4)_2,H_2PtCl_6,H_2O$ orange crystals belonging to the anorthic system (Pommerehne, *l.c.*; Krüger and Salomon, Zeitsch. physiol. Chem. 1898, 24, 364).

Derivatives. *8-Chloroparaxanthine*, m.p. 295° (corr.), soluble in 170 parts of hot water, crystallises in prisms; the *sodium salt* is sparingly, the *potassium salt* more readily soluble (Fischer and Clemm, Ber. 1898, 31, 2622); it reacts with amines to form the corresponding amino compound, and the compounds with ammonia, mono- and di-methylamine and aniline are described (Boehringer and Sohne, D. R. P. 156901). *Deoxyparaxanthine* $C_7H_{10}ON_4,H_2O$, obtained by the electrolytic reduction of paraxanthine, decomposes at 250° (Tafel and Dodt, Ber. 1907, 40, 3752), and is readily hydrolysed on heating with hydrochloric acid forming *5-methylaminomethyl-1-methyl-4-iminazalone hydrochloride*



(Tafel and Mayer, *ibid.* 1908, 41, 2546).

M. A .W.

PARAXIN. Trade name for dimethylamino-1 : 7-dimethylxanthine.

PARAZENES. A term applied to members of a series containing two benzene or similar nuclei linked together by two nitrogen atoms, each of which is attached to two para-carbon atoms in the rings. The parazenes are obtained by acting with a condensing agent on benzene or naphthalene derivatives containing an amino-group and a halogen atom in the para-position with respect to each other, and subsequently reducing the hydroxy-parazene thus produced. The members of the series are coloured compounds yielding colouring matters suitable for dyeing (Angel, Eng. Pat. 121347).

PARCHMENT. *Parchemin* (Fr.); *Pergament* (Ger.). This writing material has been known since the earliest times, but is now made in a manner very superior to that by which it was anciently prepared, as we may judge by inspection of the old vellum and parchment manuscripts. The art of making parchment consists in certain manipulations necessary to prepare the skins of animals of such thinness, flexibility, and firmness as may be required for the different uses to which this substance is applied. Though the skins of all animals may be converted into writing materials, only those of the sheep or the she-goat are used for parchment; those of calves, kids, and still-born lambs for vellum; those of the he-goat, she-goat, and wolves for drum-heads; and those of the ass for battledores. All these skins are treated in the same way, with slight variations, which need no particular detail.

They are first of all prepared by the leather-dresser. After they are taken out of the lime-pit, shaved, and well washed, they must be set to dry in such a way as to prevent their puckering and to render them easily worked. The small manufacturers make use of hoops for this purpose, but on the larger scale a *herse* or stout wooden frame is employed. This is formed of two uprights and two cross-bars solidly joined together by tenons and mortices so as to form a strong piece of carpentry, which is to be fixed against a wall. These four bars are perforated all over with a series of holes of such dimensions as to receive slightly-tapered boxwood pins truly turned, or even iron bolts. Each of these pins is transpierced with a hole like the pin of a violin, by means of which the strings employed in stretching the skin may be tightened. Above

the *herse* a shelf is placed for receiving the tools which the workman needs to have always at hand. In order to stretch the skin upon the frame, larger or smaller skewers are employed, according as a greater or smaller piece of it is to be laid hold of. Six holes are made in a straight line to receive the larger, and four to receive the smaller skewers or pins. These small slits are made with a tool like a carpenter's chisel, and of the exact size to admit the skewer. The string round the skewer is affixed to one of the bolts in the frame, which are turned round by means of a key like that by which pianos and harps are tuned. The skewer is threaded through the skin in a state of tension.

Everything being thus prepared, and the skin being well softened, the workman stretches it powerfully by means of the skewers; he attaches the cords to the skewers, and fixes their ends to the iron pegs or pins. He then stretches the skin, first with his hand applied to the pins, and afterwards with the key. Great care must be taken that no wrinkles are formed. The skin is usually stretched more in length than in breadth, from the custom of the trade, though extension in breadth would be preferable, in order to reduce the thickness of the part opposite the backbone.

The workman now resorts to the fleshing tool. It is a semicircular, double-edged knife, made fast in a double wooden handle. Other forms of the fleshing-knife edge are also used. They are sharpened by a steel. The workman holds the tool in his two hands so as to place the edge perpendicularly to the skin, and, pressing it carefully from above downwards, removes the fleshy excrescences and lays them aside for making glue. He now turns round the *herse* upon the wall, in order to get access to the outside of the skin and to scrape it with the tool inverted, so as to run no risk of cutting the epidermis. He thus removes any adhering filth, and squeezes out some water. The skin must next be ground. For this purpose it is sprinkled upon the fleshy side with sifted chalk or slaked lime, and then rubbed in all directions with a piece of pumice-stone, 4 or 5 inches in area, previously flattened upon a sandstone. The lime soon gets moist from the water contained in the skin. The pumice-stone is then rubbed over the other side of the skin, but without chalk or lime. This operation is necessary only for the best parchment or vellum. The skin is now allowed to dry upon the frame, being carefully protected from sunshine and from dust. In the arid weather of summer a moist cloth needs to be applied to it from time to time, to prevent its drying too suddenly, immediately after which the skewers require to be tightened.

When it is perfectly dry, the white colour is to be removed by rubbing it with the woolly side of a lambskin. But great care must be taken not to fray the surface—a circumstance of which some manufacturers are so much afraid as not to use either chalk or lime in the polishing. Should any grease be detected upon it, it must be removed by steeping it in a lime-pit for 10 days, then stretching it anew upon the *herse*, after which it is transferred to the *scraper*.

This workman employs here an edge tool of the same shape as the fleshing-knife, but larger and sharper. He mounts the skin upon a frame like the *herse* above described; but he extends it merely with cords, without skewers or pins, and supports it generally upon a piece of raw calfskin strongly stretched. The tail of the skin being placed towards the bottom of the frame, the workman first pares off with a sharp knife any considerable roughnesses, and then scrapes the outside surface obliquely downwards with the proper tools till it becomes perfectly smooth; the fleshy side needs no such operation; and indeed, were both sides scraped, the skin would be apt to become too thin, the only object of the scraper being to equalise its thickness. Whatever irregularities remain may be removed with a piece of the finest pumice-stone well flattened beforehand upon a fine sandstone. This process is performed by laying the rough parchment upon an oblong plank of wood in the form of a stool, the plank being covered with a piece of soft parchment stuffed with wool, to form an elastic cushion for the grinding operation. It is merely the outside surface that requires to be pumiced. The celebrated Strasburg vellum is prepared with remarkably fine pumice-stone. If any small holes happen to be made in the parchment they must be neatly patched by cutting their edges thin and pasting on small pieces with gum-water.

Another method of finishing the skin is to subject it, after a final scalding, to a bath of lime-water, and then powder it on both sides with French chalk, the excess of which is brushed off when dry. The skin is afterwards wiped over with a wet sponge and, when again dry, is rubbed over with a piece of flannel (Brand, Eng. Pat. 11693, 1893). Treatment with a bath of alum solution is said to prevent the ink soaking in and to make the parchment easier to use (Brand, *ibid.* 14384, 1894).

Parchment is coloured green only. The following is the process. In 500 parts of rain-water boil 8 of cream-of-tartar and 30 of crystallised verdigris; when this solution is cold pour into it 4 parts of nitric acid. Moisten the parchment with a brush, and then apply the above liquid evenly over its surface. Lastly, the necessary lustre may be given with white-of-eggs or mucilage of gum arabic (Ure).

PARCHMENT PAPER (*vegetable parchment*) is a modified form of paper, resembling parchment, produced by the action of sulphuric acid, zinc chloride solution or cuprammonium solutions on ordinary paper.

Manufacture by the sulphuric acid process.—The sulphuric acid used should have a density of 59°–60°B., and may be prepared by mixing 1 vol. of water with 2 vols. of ordinary strong sulphuric acid of 66°B. It is important that the temperature should not exceed 16°C. (Lotter, J. Soc. Chem. Ind. 1895, 58). The paper may contain linen or cotton fibres, or both, but regard must be had to the fact that linen is not parchmentised as quickly as cotton. The hardness of the original paper also affects the product in that a more porous paper absorbs the acid more readily and is more completely parchmentised and, therefore, more transparent. Because it is important for the acid to penetrate the fibre thick papers cannot be parchmentised, and thick vegetable parchment is made by pressing together two, three, or more sheets of thinner paper as they leave the acid bath.

After they have been washed and dried it is found that they have become perfectly united.

In the hand process the operator, wearing rubber gloves, dips the sheets of paper into the acid bath for the requisite time (2–15 seconds, according to the nature of the paper and of the product desired), and then throws them into a bath of water, from which they are passed through other wash-waters, one of which contains a small proportion of ammonia. After a final wash the sheets are dried under pressure.

In the continuous process, a band of paper passes from a roll and under glass or lead rollers in the stoneware or lead tank containing the acid at such a rate that it is immersed for the time that previous experiment has shown to be necessary for its conversion into parchment. As it leaves the bath, it passes between rubber rollers, by which the excess of acid is removed and returned to the bath, and then goes through various washing tanks, one of which contains a dilute solution of ammonia. The washing is made more complete by spraying the paper with water (*see* Arnold, Eng. Pat. 8130, 1855; J. Soc. Chem. Ind. 1885, 609). After washing, the parchment is dried by passage over heated, felt-covered rollers, and is finally calendered in the same way as ordinary papers (J. Soc. Chem. Ind. 1894, 414; *see* also Wilbaux, Eng. Pat. 17268, 1890; J. Soc. Chem. Ind. 1891, 566).

Parchment paper is sometimes rather brittle when dry, and this is overcome by impregnating it with hygroscopic substances like calcium and magnesium chlorides and glycerol (Eichorn, Eng. Pat. 5610, 1885; J. Soc. Chem. Ind. 1885, 551). Robertson has patented a continuous process in which the paper, before drying, passes through a bath of glycerol (Eng. Pat. 8473, 1892; J. Soc. Chem. Ind. 1892, 935).

Vegetable parchment may be made white and opaque and repellent to water by adding to the acid-bath white opaque pigments, *e.g.* barium sulphate, and water-repellent substances, like mineral oils (Sachsenröder, Fr. Pat. 362463, 1906; J. Soc. Chem. Ind. 1906, 713).

Manufacture by zinc chloride and cuprammonium methods.—The preparation of parchment paper by the action of a very strong solution of zinc chloride upon ordinary paper differs little from the above method, except that a longer time is required for the action, and the alkali bath is omitted from the washing.

Cuprammonium solutions (*v.* Copper) gelatinise paper in a similar way, and when the product is dried by steam-heat it is green, owing to the presence in it of copper.

Properties and uses.—The action of sulphuric acid in parchmenting paper is to convert the superficial layers of cellulose into a gelatinous mass which fills up the interstices between the fibres of the paper and renders it practically impervious to gases and liquids. During this change the paper shrinks 10–30 p.c. in area and up to 30 p.c. in thickness, and shows a corresponding increase in sp.gr. of 30–40 p.c. At the same time its strength is increased three- or fourfold and the product has about three-quarters the strength of animal parchment of the same thickness.

Good parchment paper is unaffected even by repeated soaking in boiling water and drying, and can thus be distinguished from various imitation parchment papers which are made by coating ordinary paper with size, albumin, blood serum, &c., with or without added colouring matter, and are at once disintegrated by hot water. In addition to being waterproof and gas-tight, it is unaffected by cold acids and by caustic alkalis; prolonged action of hot conc. hydrochloric acid, however, converts it into dextrin.

It is not liable to mould when damp and resists the attacks of insects, and thus possesses certain advantages over animal parchment. It takes dyes well.

It readily absorbs printer's ink and writing ink, and these cannot afterwards be erased without serious injury to the parchment. On this account it is much used for the preparation of important documents.

Vegetable parchment is also used for wrapping tobacco, &c., for luting the joints of stills, for covering jars containing preserves, &c., and for paper-bags for cooking and steaming food. It has been manufactured and used for electrical insulation (London and Bailey, Eng. Pat. 12711, 1895; *see* also L. E. Andes, The Treatment of Paper for Special Purposes).

PARIGENIN and **PARIGLIN** *v.* Sarsaparilla.

PARILLIN *v.* Glucosides and Sarsaparilla.

PARILLINIC ACID *v.* Sarsaparilla.

PARIS BLUE. This term is occasionally applied to Prussian blue, and also to the products obtained by heating aniline with stannic chloride.

PARIS GREEN. An aceto-arsenite of copper used as a pigment, and occasionally as an insecticide on plants.

PARIS LAKE. *Carmine lake v.* Lakes.

PARIS RED. A variety of rouge employed for polishing.

PARIS WHITE. *Whiting v.* Paints.

PARIS YELLOW. *Normal lead chromate v.* Chromium.

PARISITE. Fluo-carbonate of cerium metals and calcium $(CeF)_2Ca(CO_3)_2$, crystallised in the rhombohedral system. Analyses show Ce_2O_3 26–31 p.c., $(La,Di)_2O_3$ 27–30 p.c. It is found only as crystals; these usually have the form of acute hexagonal pyramids, and sometimes, when altered, show a good parting with pearly cleavage parallel to the basal plane. The colour is yellowish-brown or amber-yellow, and small crystals are often perfectly clear and transparent. Sp.gr. 4·13–4·32; H. $4\frac{1}{2}$. The mineral is found sparingly in the black limestone of the famous emerald mine near Muzo in Colombia, in granite-pegmatite at Quincy in Massachusetts, in decomposed rhyolite in Ravalli Co. in Montana, and in syenite-pegmatite in the Julianehaab district in south Greenland. Crystals from the last-named locality although at first described correctly as parisite were afterwards named synchysite.

L. J. S.

PARSLEY. *Apiin*, the glucoside of apigenin, is found in the leaves, stem, and seeds of parsley (*Carum* (*Apium*) *petroselinum*, Benth. and Hook.), (Rump, Buchner's Repert. f. Pharm. 1836, 6, 6; Braconnot, Ann. Chim. 1843, iii. 9, 250). Both authors obtained it as a

gelatinous mass by extracting parsley seeds with boiling water, and considering the readiness with which it gelatinised. Braconnot included it among the members of the pectin class. Subsequently, Planta and Wallace assigned to it the formula $C_{24}H_{28}O_{13}$ (Annalen, 1850, 74, 262), and though by the action of boiling dilute acids a brown substance, $C_{24}H_{20}O_9$, was produced, it did not appear that apiin was a glucoside. On the other hand, Linderhorn (Inaugural Dissert. Wurzburg, 1867), who obtained this substance in a crystalline condition, found that by the action of dilute acids it was decomposed into glucose and apigenin, and that the reaction probably proceeded as follows:—

$$C_{12}H_{14}O_7+H_2O=C_6H_4O_2+C_6H_{12}O_6$$

Von Gerichten (Ber. 1876, 9, 1124), who found for apiin and apigenin numbers identical with those given by Lindenhorn, showed that on fusion with alkali apiin gave *phloroglucinol* and an acid not closely examined, but which, by the further action of the alkali, gave *protocatechuic acid* besides some *oxalic*, *formic*, and *para-hydroxybenzoic acids*. As a result of his investigation, von Gerichten considered the most probable formula for apigenin to be $C_{15}H_{10}O_5$, and that the decomposition of the glucoside with acids might be represented as follows:—

$$C_{27}H_{32}O_{16}+H_2O=2C_6H_{12}O_6+C_{15}H_{10}O_5$$

In a later communication (Annalen, 318, 124), however, he adopted the formula

$$C_{26}H_{28}O_{14}\cdot H_2O$$

as he found that on hydrolysing apiin with $\frac{1}{2}$ per cent. sulphuric acid it is converted into *apiose* and *glucose apigenin*—

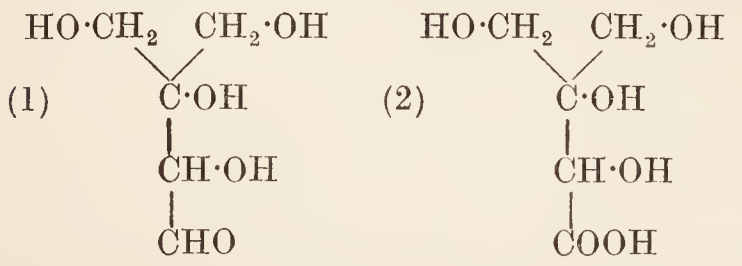
$$C_{26}H_{28}O_{14}+H_2O=\underset{\text{Apiose.}}{C_5H_{10}O_5}+\underset{\text{Glucose apigenin.}}{C_6H_{11}O_6\cdot C_{15}H_9O_4}$$

By the prolonged action of the acid, the latter compound gives apigenin and glucose—

$$C_6H_{11}O_6\cdot C_{15}H_9O_4+H_2O=C_6H_{12}O_6+C_{15}H_{10}O_5$$

Apiin therefore contains a disaccharose nucleus which on hydrolysis yields dextrose and apoise.

Apiose is an aldopentose of the formula (1), and on oxidation gives *apionic acid* (2)—



By the action of hydriodic acid and phosphorus, apionic acid is reduced to *iso*-valeric acid.

When apiin is boiled with nitric acid in 60 p.c. acetic acid it is converted into the nitromonoglucoside *nitroapigetrin* $C_{21}H_{21}O_{11}NO_2$, a yellow crystalline powder, m.p. 254°–255°, soluble in alkaline solutions with a yellow colour (Perkin, Chem. Soc. Trans. 1900, 416, 77).

Apiin forms colourless needles, m.p. 228°, easily soluble in hot water and alcohol. From these solutions it separates on cooling in the gelatinous condition.

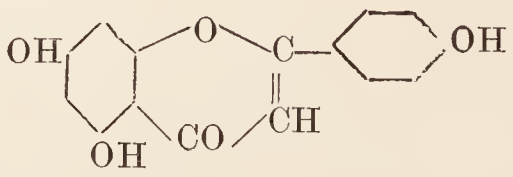
Whereas apiin can be most readily obtained in a pure condition from the seeds of parsley, it has been shown by von Gerichten that the stem and leaves of this plant contain in addition a glucoside of a *luteolin monomethylether*. By fusion with alkali, pure apigenin gives phloroglucinol and p-*hydroxybenzoic acid* (Ber. 1900, 33, 2334). The previous isolation of *protocatechuic acid*, according to this method by von Gerichten, and Perkin (Chem. Soc. Trans. 1897, 71, 805), was due to its contamination with a trace of this luteolin derivative.

In order to prepare apigenin, Perkin (*l.c.*) digests 30 grams of apiin for twenty hours with 3 litres of hydrochloric acid (sp.gr. 1·04). The crude colouring matter is extracted with boiling alcohol, and the extract treated with alcoholic lead acetate solution, drop by drop, until the supernatant liquid becomes colourless. The lead precipitate is then removed, and the filtrate after treatment with a few drops of acetic acid is evaporated to a small bulk. By addition of a little boiling water and gentle evaporation, the apigenin separates in a crystalline condition.

Should the substance be contaminated with luteolin monomethylether, it is digested for two hours with boiling hydriodic acid (sp.gr. 1·96) and the product crystallised from alcohol. The more soluble luteolin thus formed remains in solution (Czajkowski, v. Kostanecki, and Tambor, Ber. 1900, 33, 1996).

Apigenin thus prepared crystallises in almost colourless leaflets, m.p. 343°, and dissolves in alkaline solutions with a yellow coloration. By means of acetic anhydride *triacetyl-apigenin*, colourless needles, m.p. 181°–182°, is produced (Czajkowski, v. Kostanecki, and Tambor), but when methylated by means of methyl iodide, only a *dimethylether* $C_{15}H_8O_2(OCH_3)_2$, pale yellow needles, m.p. 171°–172° (Perkins, *l.c.*), can be prepared. On acetylation this yields *acetylapigenin dimethylether*, colourless needles, m.p. 195°–196° (Perkin), and by means of alcoholic potash is transformed into a yellow potassium salt which is decomposed by washing with water. When hydrolysed with alcoholic potash, apigenin dimethylether yields *anisic acid* and a syrupy phenolic substance, which probably contains *phloroglucinol monomethylether*.

If apigenin is digested with 50 p.c. potassium hydroxide solution, it is hydrolysed with formation of p-*hydroxyacetophenone* and phloroglucinol (Perkin, *l.c.*). From the result of his investigation, Perkin assigned to apigenin the constitution of a *hydroxychysin*, or 1 : 3 : 4′ : *trihydroxyflavone*—

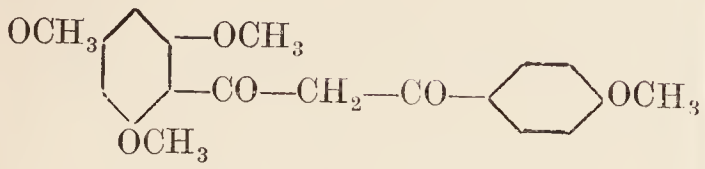


Somewhat later, Czajkowski, v. Kostanecki, and Tambor (*l.c.*) synthesised apigenin by a series of reactions similar to those employed for the preparation of chrysin (Emilewicz, v. Kostanecki, and Tambor, Ber. 32, 2448).

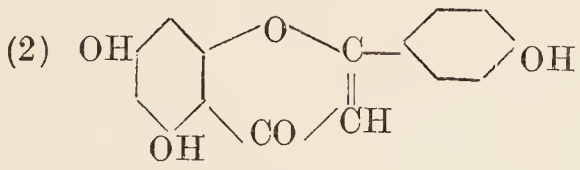
Phloracetophenone trimethylether condensed with *ethyl anisate* in the presence of sodium gives *tetramethoxybenzoylacetophenone* (1), and this on

boiling with hydriodic acid is converted into apigenin (2)—

(1)



(2)



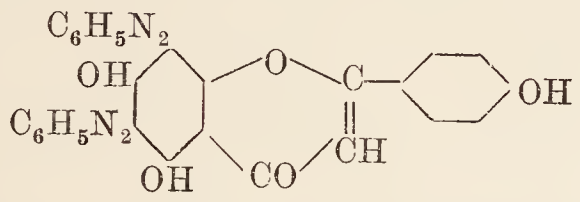
The following derivatives of apigenin have been prepared:—

Apigenin diethylether $C_{15}H_8O_3(OC_2H_5)_2$, yellow needles, m.p. 161°–162° (Perkin), 163°–164° (Czajkowski, v. Kostanecki, and Tambor); *acetylapigenin diethylether*

$$C_{15}H_7O_3(OC_2H_5)_2{\cdot}C_2H_3O$$

colourless needles, m.p. 151°–152° (Perkin), 148°–149·5° (Czajkowski, v. Kostanecki, and Tambor); *tribenzoylapigenin* $C_{15}H_7O_5(C_7H_5O)_3$, colourless needles, m.p. 210°–212° (Perkin); *dibromapigenin* $C_{15}H_8Br_2O_5$, pale yellow needles; *mononitroapigenin* $C_{15}H_9O_5(NO_2)$, orange-yellow prismatic needles; *trinitroapigenin* $C_{15}H_7O_5(NO_2)_3$, minute yellow needles; and *tetranitroapigenin* $C_{15}H_6O_5(NO_2)_4$, almost colourless needles, m.p. 243°–244° (decomp.).

Disazobenzene-apigenin crystallises in red needles (Perkins, *l.c.*), m.p. 290°–292° (decomp.)



and with acetic anhydride gives only the monoacetyl-derivative $C_{15}H_7O_5(C_2H_3O)(C_6H_5N_2)_2$, orange-red needles, which commence to decompose at 260° and melt at about 277°–280°.

Apigenin closely resembles chrysin in its tinctorial properties, although it is a somewhat stronger dyestuff. The shades it gives upon wool mordanted with aluminium, chromium, and iron are respectively pure yellow, weak yellow-orange, and chocolate-brown.

Apigenin is also present in weld (*Reseda luteola*), (Perkin and Horsfall, Chem. Soc. Trans. 1900, 77, 1314), in the flowers of *Antirrhinum majus* (Wheldale and Bassett, Biochem. Journ. 1913, 7, 441), and exists probably also in camomile flowers (Perkin). A. G. P.

PARSLEY, OIL OF, *v.* OILS, ESSENTIAL.

PARSNIP, *Peucedanum sativum* (Benth. and Hook). The tap root is used as a vegetable. König gives as the average composition—

Water	Protein	Fat	Sugar	Other N-free subst.	Crude fibre	Ash
83·2	1·4	0·4	2·3	8·1	3·6	1·0

It has also been used as a root crop for the feeding of horses, cows, and bullocks. The yield is from 12 to 24 tons per acre, and the material possesses higher feeding value than turnips, mangolds, or carrots (Guépin, Ann. Agron, 1900, 26, 476). The ash is rich in potash (42 p.c.). H. I.

PARTING. The separation of gold and silver by means of nitric acid, *v.* ASSAYING.

PARTINIUM. An alloy of aluminium and tungsten used in automobile construction.

PARVOLINE $C_5HN(CH_3)_4$. A homologue of pyridine.

PASCOITE. A hydrated vanadate of calcium, $2CaO{\cdot}3V_2O_5{\cdot}11(?)H_2O$, crystallised in the monoclinic (?) system. It occurs as an orange-red or orange-yellow, powdery efflorescence on the walls of the workings in the vanadium mine at Minasragra, near Cerro de Pasco-Peru, where it has resulted from the alteration of patronite (*q.v.*). Sp.gr. 2·457. The mineral melts readily to a dark red liquid, and it is soluble in water. L. J. S.

PASTES *v.* GEMS, IMITATION.

PATCHOULI CAMPHOR *v.* CAMPHOR; also OILS, ESSENTIAL.

PATCHOULI OIL *v.* OILS, ESSENTIAL.

PATENT LEATHER VARNISH *v.* VARNISH.

PATENT PHOSPHINES *v.* ACRIDINE DYESTUFFS.

PATERAITE *v.* MOLYBDENUM.

PATINA. The green film which forms upon bronze and copper mouldings, and consisting of basic copper carbonate. On bronze statues it produces a pleasing effect owing to its colour, smoothness, and transparency, so that the bronze itself may be seen through it in places. The conditions which favour the formation of patina are a pure atmosphere, the presence of moisture in the air or in the earth where the articles may have lain buried, and a smooth surface. The finest examples of patina are found upon bronzes of ancient manufacture in which much tin and little zinc were used as alloy. The effect of a natural, and consequently slowly formed coating of patina is frequently imitated artificially by wetting articles of bronze with dilute acids.

PATRONITE. A vanadium sulphide (VS_4 or V_2S_2+nS), forming a large deposit in the Quisque (or Minasragra) district, near Cerro de Pasco in Peru. It is amorphous and dull with a black or very dark greenish-black colour, and somewhat resembles asphaltum in appearance. Analyses show 15 to 24·8 p.c. of vanadium with combined sulphur and various impurities (silica, alumina, free sulphur, carbonaceous matter, &c.). Sp.gr. 2·65-2·71. Banded with vanadiferous asphaltum, quisqueite (*q.v.*), and a coke-like material, it forms a large vein or lenticular mass in red shales of Cretaceous age which are penetrated by dykes of igneous rock. This deposit has been extensively mined; the material is roasted to drive off volatile constituents, and the residue exported for the manufacture of vanadium steel. W. Lindgren (Amer. J. Sci. 1922, iii. 195) suggests that patronite is a mixture of three different minerals. (*See* W. F. Hillebrand, Amer. J. Sci. 1907, xxiv. 141; D. F. Hewett, Trans. Amer. Inst. Mining Engin. 1910, xl. (1909), 274.) (*v.* VANADIUM.) L. J. S.

PAUCINE $C_{27}H_{39}O_5N_5$, obtained from the seeds of *Pentaclethra macrophylla* (Benth.) sometimes imported from West Africa as an oil-seed ('Owala beans'). Yellowish leaflets with $6\frac{1}{2}H_2O$, m.p. 126°. Salts crystalline. Poisonous (Merck's Bericht, 1894, p. 11).

PAULLINITANNIC ACID *v.* GUARANA.

PAVIIN *v.* HORSE CHESTNUT.

PAWLOWNIA OIL. An oil obtained in Japan from the kernels of the nuts of *Aleuritis*

cordata, in which it occurs to the extent of 49 p.c. The tree grows wild on the coast of the Japan Sea, on the main island, and is now being cultivated to a small extent. It is used locally in the manufacture of oil-paper and paints and for illuminating purposes.

PAWPAW, *Cariac Papaya* (Linn.). The fruit is edible. According to Prinsen Geerligs (Chem. Zeit. 1897, 21, 719), the following figures give its average constitution :—

Average wt. of 1 fruit	Flesh	Rind	Seeds
600 grammes	65	10	25 p.c.

The flesh contains—glucose, 2·6 p.c.; fructose, 2·1 p.c.; cane sugar, 0·9 p.c.

Of more importance is the occurrence in the juice of the fruit of an enzyme—*papayin* or *papain*—which resembles pepsin. In the West Indies this juice is collected by making incisions in the fruit while still on the tree, with a bone or wooden knife, and receiving the juice in earthen or glass vessels. The juice, which rapidly coagulates to a white curd, is very putrescible, and has therefore to be rapidly dried, either in the sun or by artificial heat, care being taken not to raise the temperature much above 35°–40° (*v.* PAPAIN). H. I.

PAYTAMINE and **PAYTIME** *v.* QUEBRACHO ALKALOIDS.

PEA. The garden pea, *Pisum sativum* (Linn.), is a leguminous plant, growing in temperate climates. The seeds are used largely as human food in the green immature condition and also when ripe and dry.

The air-dried ripe seeds, on the average, contain (König)—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
13·6	23·4	1·9	52·7	5·6	2·8

Of the total nitrogen in peas, non-proteid nitrogen constitutes from 8 to 11·5 p.c. The proteids have been investigated by Osborne and Campbell (J. Amer. Chem. Soc. 1896, 18, 583; *ibid.* 1898, 20, 348 and 410), who find them to consist of *legumin* and *vicilin*, together amounting to about 10 p.c., *legumelin* about 2 p.c., and two other substances, *protoproteose* and *deuteroproteose*. Legumin is a globulin not coagulated at 100° and containing 16·75 p.c. nitrogen and 0·46 p.c. sulphur; vicilin is a similar substance, but coagulates at 95° and contains 17·15 p.c. nitrogen and only 0·1 to 0·2 p.c. sulphur; legumelin is an albumin, coagulates below 80° and resembles the leucosin of wheat (Osborne and Harris, J. Biol. Chem. 1907, 3, 213). For description of the hydrolysis of these proteids, *v.* Osborne and Heyl, J. Biol. Chem. 1908, 5, 187.

Choline and trigonelline have been found in peas (Schulze and Frankfurt, Ber. 1894, 27, 769).

The nitrogen-free extract contains about 68 p.c. of starch, 10·5 p.c. of dextrin, &c., and 4 p.c. of pentosans. The fat is a pale-yellow oil, containing much lecithin and some phytosterol.

Green peas—the unripe form in which the seeds are usually eaten as a vegetable—contain on the average—

Water	Protein	Fat	Sugar and other N-free subst.	Crude fibre	Ash
77·7	6·6	0·5	12·4	1·9	0·9

The nitrogenous matter consists largely of non-proteid bodies, 25–33 p.c. of the total nitrogen being in this form.

The ash of peas contains—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
41·8	1·0	5·0	8·0	0·9	36·4	3·5	0·9	1·5

Bottled and canned green peas are largely prepared, and in many cases the colour is rendered brighter by the use of copper compounds, added either by actual addition of some copper salt or by boiling the peas in a copper vessel. According to Tschirch, an insoluble phyllocyanate of copper, $Cu(C_{24}H_{27}N_2O_4)_2$ is produced in the tissues of the pea by such treatment; 50 milligrams of copper per kilogramme of peas is said to be sufficient to impart a permanent and adequate greenness to peas, and twice this amount is permitted by law in France and Italy (Wynter Blyth). Such addition of copper is illegal in England.

The field pea, *Pisum arvense*, is an important farm crop, the seed furnishing an excellent and richly nitrogenous food for fattening stock, while the power of collecting nitrogen from the air, which peas in common with other *leguminosæ* possess, serves to enrich the soil on which it is grown.

The following analyses by Kellner show the average composition of field peas :—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Green plant, flowering	84·6	4·0	0·5	5·1	4·5	1·4
Hay, cut in flower	16·7	14·3	2·6	34·2	25·2	7·0
Straw, cut when ripe	13·6	9·0	1·6	33·7	35·5	6·6
Seeds, air-dried	14·0	22·5	1·6	53·7	5·4	2·8
Husks	12·0	7·3	1·2	31·9	44·7	2·9
Bran	11·7	16·8	1·7	46·2	20·1	3·5
Feeding meal	13·5	23·4	2·0	51·0	7·0	3·1

H. I.

PEA IRON ORE *v.* IRON.

PEA-NUT, Earth-nut or **Ground-nut,** *Arachis hypogæa* (Linn.) the seed of a plant growing in warm climates. After flowering, the stalk bends over and enters the soil, where the seeds grow and ripen. The seeds are contained in paper-like pods, or husks, and there are usually two, though in some varieties four, seeds in each pod.

The average composition of the shelled seed is given by König as—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
7·5	27·5	44·5	15·7	2·4	2·5

The writer has found in samples of Transvaal pea-nuts considerably higher proportions of oil, *e.g.* the following three analyses may be quoted (A grown in the Transvaal from Virginian seed; B grown in the Transvaal from Spanish seed; C imported seed, variety 'Mammoth') :—

100 pods of A weighed 155·4 grammes and contained 169 kernels;

100 pods of B weighed 102·4 grammes and contained 170 kernels;

100 pods of C weighed 190·3 grammes and contained 288 kernels.

A consisted of 66 p.c., B of 76·4 p.c., and C of 71·6 p.c. kernel.

The kernels, on analysis, gave the following :—

	A	B	C	
Moisture	4·88	5·05	4·37	p.c.
Protein	30·13	31·19	24·82	,,
Oil	46·06	46·08	54·35	,,

The seeds, after roasting, possess an agreeably nutty flavour, and are used to some extent as human food. They are of more importance as a source of oil (*v.* ARACHIS OIL, also art. OILS, FIXED, AND FATS), while the press cake left is a valuable cattle food containing, according to Kellner :—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
9·8	44·5	9·2	23·8	5·2	7·5

Samples containing up to 50 p.c. protein are not uncommon, and, if the seeds are free from sand, the ash is lower than the figures given.

The protein of the pea-nut contains two globulins—*arachin*, C 52·15, H 6·93, O 22·23, N 18·29, S 0·40 p.c.; and *conarachin*, C 51·17, H 6·87, O 22·58, N 18·29, S 1·09 p.c. The latter contains 6·55 p.c. of basic nitrogen, the highest known in any seed protein. Pea-nut cake, therefore, should be highly valuable in supplementing cattle foods made from cereals, &c., where the proteins are deficient in basic amino-acids (Johns and Jones, Bio-Chem. J. 1916, 28, 77).

In a later paper (Bio-Chem. J. 1917, 30, 33) the same authors state that the globulins contain arginine, histidine, and lysine. Arachin contains 5 p.c. and conarachin 6 p.c. of lysine.

The 'vines,' after removal of the seed, may be used as hay for cattle. American analyses show them to contain—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
10·0	10·0	3·6	42·0	22·0	12·4

For a description of the cultivation and applications of the pea-nut or 'pindars' in Jamaica, *see* J. Imp. Inst. 1898, Dec. 341.

H. I.

PEACH, *Prunus Persica* (Stokes), a tree growing in warm climates, bearing a fruit which is valued for table purposes. Many varieties are known; they may be divided into two types—cling-stone and free-stone peaches, according to the character of the connection between the flesh and the stone or 'pit' of the fruit.

König gives as the average composition—

Water	Protein	Free acid	Invert sugar	Cane sugar	Other N-free ext.	Fibre	Ash
82·0	0·9	0·7	3·7	4·5	1·2	6·5	0·6

Under 'fibre' in the above figures is included the stone, which constitutes from 4·6 to 6·8 p.c. of the whole fruit. About 0·8 p.c. of pentosans is present. The peach kernel contains a fixed oil, amygdalin, and a proteid, *amandin* (Osborne and Campbell, J. Amer. Chem. Soc. 1896, 18, 609). For changes in composition during ripening, *v.* Bigelow and Gore (J. Amer. Chem. Soc. 1905, 27, 915).

The juice of peaches has a sp.gr. of about 1·05, contains 13 p.c. of total solids, including 2 p.c. invert sugar, 7 p.c. of cane sugar, and 0·6 p.c. free acid (as malic acid). It can readily be fermented, and is used as a source of alcohol—so-called peach brandy. The odorous constituents of the pulp of the ripe peach consist chiefly of the linalyl esters of formic, acetic, valeric, and caprylic acids, together with acetaldehyde and furfural. Probably the volatile acids are present to some extent in the free state. The yield of essential oil is about 0·00074 p.c. of the fresh pulp. The oil is very unstable and on exposure to air loses its fragrance (Power and Chestnut, J. Amer. Chem. Soc. 1921, 43, 1725).

Peaches are often preserved by drying or canning in syrup. American analyses of canned peaches show them to contain—

Water	Protein	Fat	N-free extract and fibre	Ash
88·1	0·7	0·1	10·8	0·3

H. I.

PEACH KERNEL, OIL OF, *v.* OILS, ESSENTIAL; *also* OILS, FIXED, AND FATS.

PEACH WOOD *v.* BRAZIL WOOD.

PEACOCK-COPPER ORE *v.* COPPER-PYRITES.

PEAR, *Pyrus communis* (Linn.). Many varieties are known. The average composition of the ripe fruit is given by König as—

Water	Protein	Free acid	Invert sugar	Cane sugar	Other N-free extract	Fibre and pips	Ash
83·8	0·4	0·3	7·1	1·5	3·4	2·8	0·3

A considerable quantity of pectin and pectous substances is present. Pear juice, like apple juice, readily ferments and yields an alcoholic liquid—perry—resembling cider. From this a brandy can be prepared (*v.* Windisch, Zeit. Spiritusind. 1905, 2887). Tannin is present, especially in the rind (Kehlhofer, Bied. Zentr. 1900, 29, 248). The rind also contains a wax melting at 68° (Seifert, Landw. Versuchs. Stat. 1894, 45, 29). The dried seeds of pears were examined by Huber (Landw. Versuchs. Stat. 1911, 75, 443), who found them to contain—

Fat	Sugar	Furfuroids	Crude fibre	Protein	Amides	Ash
25·0	5·4	6·7	9·0	5·4	0·2	3·8

The leaves of pear trees contain from 1·2 to 1·4 p.c. of a glucoside (m.p. 194°), which, on hydrolysis, yields quinol, and is probably identical with arbutin (Bourquelot and Fichtenholz, Compt. rend. 1910, 151, 81). The existence of quinol in the buds of pear trees was observed by Rivière and Bailhache (Compt. rend. 1904, 139, 81).

The ash of pears (whole fruit) was found by Wolff to contain—

K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	SiO_2
54·7	8·5	5·2	8·0	15·3	5·7	1·5

Pears are sometimes dried, but more generally preserved by canning. American analyses give the following :—

	Water	Protein	Fat	Total carbohydrates	Ash
Dried pears .	16·5	2·8	2·4	72·9	2·4
Canned pears	81·1	0·3	0·3	18·0	0·3

H. I.

PEARCEITE *v.* POLYBASITE.

PEARL ASH. A variety of potassium carbonate, *v.* POTASSIUM.

PEARL-HARDENING (*Satin spar*, *Satinite*, or *Annaline*) is the trade name for artificial crystallised calcium sulphate. It may be prepared by treating calcium chloride solution with dilute sulphuric acid; by boiling waste gypsum with hydrochloric acid (Eng. Pat. 1577, 1897), or by the double decomposition of sodium or magnesium sulphate with calcium chloride (Eng. Pat. 7797, 1891). It is used in paper manufacture as a filling for writing paper (*v.* CALCIUM).

PEARL SINTER. A kind of opal found in the cavities of volcanic tufa.

PEARL SPAR *v.* DOLOMITE.

PEARL WHITE is (1) a basic bismuth nitrate or oxychloride (*v.* BISMUTH); (2) a preparation of mother-of-pearl.

PEARLITE. The name given by Sorby (J. Iron and Steel Inst. 1886, 140; 1887, 255) to the eutectic mixture of ferrite and cementite present in steels. It may consist of alternate lamellæ of the constituents, which with oblique light show iridescent colours like mother-of-pearl, or it may exist in granular or 'beady' forms (Benedicks, Métallurgie, 1909, 6, 567). The two constituents are identical with 'free' ferrite and cementite (Ledebur, Stahl u. Eisen, 1887, 8, 742; 1891, 11, 294).

It is the principal, sometimes the only constituent of intermediate steels and under the microscope is characterised by polishing in relief or etching, when the cementite stands out from the softer ferrite.

PEARLS. Calcareous concretions formed by various molluscs, those used in jewellery being mostly obtained from the large pearl-oyster, *Meleagrina margaritifera* (Lam.), belonging to the family *Aviculidæ*. The material and structure of a pearl are identical with those of the mother-of-pearl (*q.v.*) lining of the shells. The analysis of several fine white pearls by Harley gave calcium carbonate, 91·72; organic matter, 5·94; water, 2·23 (Proc. Roy. Soc. 1888, 43, 461). The calcium carbonate is of the orthorhombic modification identical with the mineral aragonite, and the organic matter is chiefly conchiolin. The sp.gr. of pearls varies between 2·650 and 2·686; and the hardness is nearly 4 on the mineralogical scale. Most pearls present a concentric structure, having been formed by successive deposits around a nucleus. This nucleus is in all cases the body of a minute parasite, the larva of a tapeworm, which in its adult state lives in the fishes and ducks that feed on the oysters and fresh-water mussels. The irritation caused by the parasite stimulates the secretion of nacre by the mollusc. A pearl is thus the brilliant sarcophagus of a parasite. The pearls are usually found in the mantle, but sometimes in the muscles of the mollusc; or, having escaped from the tissues, they may become adherent to the shell. To be valued by the jeweller, the pearl should be of spherical form, while its skin or outer coat should display the delicate iridescent sheen known as the 'orient.' Pearls of more or less hemispherical shape, cut from the shell, are termed *boutons*; while those which are warty or irregular in form pass under the name of *baroque*. Occasionally a pearl is found completely embedded in the mother-of-pearl. Some pearls, instead of showing a concentric structure, are crystalline, being composed of striated prisms radiating from the centre, and these may or may not possess a nucleus (Harley Proc. Roy. Soc. 1889, 45, 612).

The principal pearl fisheries are those of Torres Straits and the north-west coast of Western Australia, the Sulu Archipelago, Ceylon and the coast of Madras, the Persian Gulf, and the Gambier and Pomotou Islands. The American fisheries are chiefly in the Caribbean Sea, off the coast of California, and near Panama; here the pearls are mostly derived from *Meleagrina California* (W. H. Dall, Amer. Nat. 1883, 17, 579, 731; E. W. Streeter, Pearls and Pearling Life, London, 1886).

Coloured pearls are occasionally found, the tint in each case being dependent on that of the nacre lining the shell. The highly-prized black pearls are obtained chiefly from Mexico, and it has been suggested that the colour is due to the presence in the water of salts of silver, derived from neighbouring silver mines. Pearls have been artificially stained by means of silver salts. Pink pearls, sometimes finely water-lined, are mostly derived from the conch shell *Strombus gigas*; while large, coarse, yellowish pearls are obtained from the great clam, *Tridacna gigas*.

The principal source of fresh-water pearls is the pearl-mussel (*Unio margaritiferus*), a mollusc widely distributed in the rivers of northern temperate regions. It is found in the Tay, Forth, Earn, Doon, and many other mountain streams in Scotland. Scottish pearl-fishing was revived in 1860, and successfully carried on for some years. The pearl-mussel is also found in Cumberland; in Wales, especially in the Conway; and in Ireland. On the Continent pearl-fishing has been prosecuted in Saxony, Bohemia, and Bavaria; and in Norway, Sweden, and even Lapland. The American rivers also yield pearl-bearing molluscs, especially in New England, New Jersey, and Ohio; and in Canada (G. F. Kunz, Gems of N. America, New York, 1890). Fresh-water pearls are likewise obtained from China and Japan, and the Chinese exhibit much skill in inducing the formation of pearl by the artificial introduction of certain objects, upon which the mollusc deposits a nacreous layer. Chinese shells with images of Buddha formed of pearl adherent to the inner surface are well known to collectors (D. T. Macgowan, Journ. Soc. Arts, 1853, 2, 72; F. Hague, J. Roy. Asiatic Soc. 1856, 16).

The 'culture' pearls produced at K. Mikimoto's pearl culture farm in the Bay of Ago, Japan, are oyster-made pearls grown under controlled conditions. A small pearl ('seed' pearl) or a bead of nacre is inserted by a surgical operation into the mantle of the mollusc, care being taken that it is surrounded by a layer of the nacre-secreting epidermis. The oyster is then returned to the sea-bed for a period of at least four years, when the foreign body becomes coated naturally with successive layers of nacre. Such a pearl cannot be distinguished externally from a pearl that has been produced under wholly natural conditions, and, of course, the two are identical chemically. When, however, a 'culture' pearl is sawn through the centre (thereby destroying its value) the nucleus is revealed. The Japanese also produce pearl beads by skilfully cementing together two hemispherical button pearls.

Imitation pearls are manufactured on the Continent in a variety of ways. Some are globes of thin opaline glass, filled with gum or wax, and deadened on the surface by means of hydrofluoric acid. The better kinds are glass globules lined with a nacreous composition, formed by digesting the silvery scales of the bleak in ammonia. Roman pearls are glass spheres, to which the nacreous material is applied externally. Celluloid, incorporated with

fish scales, has become a favourite material for imitation pearls. Black pearls have been imitated by beads of a very compact hæmatite, which may be polished so as to present a kind of plumbago-lustre. Pink pearls are frequently confounded with beads of pale coral.

The so-called cocoa-nut pearls, from the Malay Archipelago, are pearl-like bodies, resembling ivory, said to be found inside cocoa-nuts. Certain bodies which have been described as mammalian pearls are simply biliary concretions, formed mainly of cholesterol.

Ref.—W. A. Herdman and J. Hornell, Rep. Ceylon Pearl Fisheries (Roy. Soc. London, 1903); G. F. Kunz and C. H. Stevenson, The Book of the Pearl (New York, 1908); M. Bauer, Precious Stones (transl. by L. J. Spencer) (London, 1904); K. Möbius, Die echten Perlen (Hamburg, 1857); H. L. Jameson, The Japanese artificially induced Pearls, Nature, 1921, cvii. 396, 621. L. J. S.

PEASTONE v. Oolite.

PEAT and **TURF** *v.* Fuel.

PEATWAX *v.* Waxes.

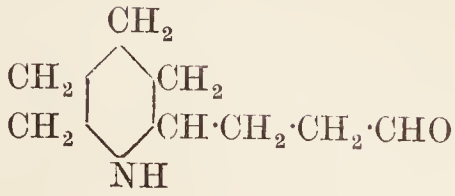
PECTIN. A substance present in fruits, and in the carrot, turnip, &c. A solution of pectin in presence of sugar and an acid forms a gel on which property the 'setting' of jellies and jams is due. Pectin separates as a gelatinous precipitate when alcohol is added to an aqueous extract of a fruit. On treatment with alkali it yields *pectic acid*, methyl alcohol, and acetone. Lippmann (Biochem. Zeitsch. 1920, 106, 236) attributes the methyl alcohol found in rum to the decomposition of the pectin of the sugar cane. Methyl alcohol and acetone are present in cider, being derived from the pectin of the apple juice. The methyl alcohol and acetone are probably present in pectin as ester groupings, the acetone occurring as an ester of its enolic modification, *iso*propenyl alcohol, $CH_3 \cdot C(OH) : CH_2$. Hence it would appear that pectin is the dimethyl*iso*propenyl ester of pectic acid (Tutin, Bio-Chem. J. 1921, 15, 494).

PELARGONIC ACID *v.* Nonoic acids.

PELARGONIDIN, PELARGONENIN, PELARGONIN *v.* Anthocyanins. *Cf.* Currey, Chem. Soc. Trans. 1922, 319.

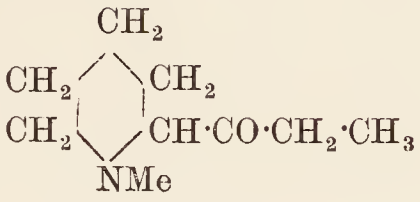
PELLETIERINE and the alkaloids of Pomegranate Bark. The root-bark of *Punica granatum* (*Granati cortex*, B.P.; *Granatum*, U.S. P.) is used against tape worms, and contains, according to Tanret (Compt. rend. 1878, 86, 1270; 1879, 88, 716; 1880, 90, 696), four alkaloids, to which a fifth, *iso*methylpelletierine, was added by Piccinini (Gazz. chim. ital. 1899, 29, 311). Two of these five were regarded as optically active forms of two others, but according to Hess (Ber. 1917, 50, 368; 1919, 52, 964, 1005, 1622; Hess and Eichel, *ibid.* 380, 1192, 1386; 1918, 51, 741) no optically active alkaloids occur in the bark; Tanret has reaffirmed (Compt. rend. 1920, 170, 1118) the optical activity of pelletierine, $[\alpha]_D -31{\cdot}1°$ and of methylpelletierine, $[\alpha]_D +27{\cdot}7°$ and states that these alkaloids are very easily racemised by heat, by acids and by bases. Hess uses a slightly different nomenclature to previous workers, which is here adopted, as he has established the constitution of the alkaloids concerned.

Pelletierine (*iso*pelletierine of Tanret) $C_8H_{15}ON$ is a liquid, sp.gr. 0·988 at 0°; it darkens and



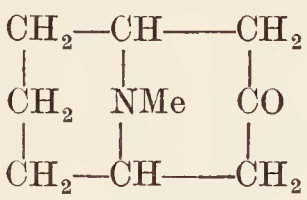
resinifies in air; b.p. 195° under atmospheric pressure, 106°/21 mm. Soluble in 23 parts of water at 15°, giving a strongly alkaline solution. It is the aldehyde of *d.l*-coniine, which it yields on reduction and closely resembles in properties. Hess and Eichel have resolved it by means of the tartrate. (According to Tanret, pelletierine is optically active, and *iso*pelletierine is the corresponding racemic base.) The hydrochloride, m.p. 143°–144°, is not hygroscopic when pure; the hydrobromide crystallises extremely well, m.p. 140°.

Methyl*iso*pelletierine $C_9H_{17}ON$ is identical with Tanret's methylpelletierine and also with Piccinini's *iso*methylpelletierine; it is, however, not a methyl derivative of pelletierine, but of an unknown *iso*meride. It is the N-methyl derivative of



the ketone corresponding to conhydrine (*v.* Conium alkaloids), from which it can be prepared by oxidation and methylation. Methyl*iso*pelletierine boils at 114°–115°/24 mm.; the hydrobromide forms long needles, m.p. 151°–152°. Like pelletierine, methyl*iso*pelletierine has been resolved by Hess and Eichel. These authors (Ber. 1917, 50, 380) have found in the bark a minute quantity of a new alkaloid, isomeric with the last named, in which the keto group is in the β position of the side chain b.p. 101°–103°/19 mm. Later Hess (Ber. 1919, 52, 964) has invoked the presence of an asymmetric tervalent nitrogen atom to explain the isomerism.

Pseudopelletierine $C_9H_{15}ON, 2H_2O$ has for some years been recognised as a ring homologue of tropinone (*v.* Solanum alkaloids, Atropine) of the annexed constitution. (Ciamician and Silber



Ber. 1892, 25, 1601; 1893, 26, 156, 2740; 1894, 27, 2851; 1896, 29, 492; Piccinini, Gazz. chim. ital. 1899, 29, i. 408; ii. 115; 1901, 31, i. 561; Willstätter and Veraguth, Ber. 1905, 38, 1984.) It is the only solid alkaloid in the bark, m.p. 53°–54°, b.p. 140°/20 mm., 246°/760 mm.

The *extraction* of the alkaloids is effected by mixing the powdered bark with milk of lime, extracting with water, shaking into chloroform and then into sulphuric acid. The separation is affected by fractional extraction with chloroform from sodium bicarbonate and then from caustic soda solution (*v.* Tanret, Piccinini).

The bulk of pelletierine, the principal alkaloid, is isolated as hydrobromide, and the residual oily alkaloids are fractionally distilled *in vacuô*. A new scheme has been described by Hess and Eichel (Ber. 1917, 50, 1386) who convert the secondary base pelletierine with ethylchlorocarbonate into the urethane of a much higher boiling-point.

For the *estimation* (based on extraction with ether and sodium hydroxide) *see* Ewers (Arch. Pharm. 1899, 237, 49) and German Pharmacopœia V. which demands a minimum content of 0·4 p.c. in the bark. According to Ewers the bark may contain 0·63–0·72 p.c. of which nearly one half consists of pelletierine, the chief anthelmintic alkaloid. Carr and Reynolds (Pharm. J. 1908, [iv.] 26, 542) found in a large number of commercial specimens only 0·12–0·29 p.c. of alkaloid. Hess (Ber. 1919, 52, 1005) found: pelletierine 0·0525 p.c., pseudo-pelletierine 0·179 p.c., methyl-*iso*-pelletierine 0·022 p.c., *iso*pelletierine 0·0015 p.c. and α-1-methyl-piperidyl-propane-β-one 0·001 p.c. G. B.

PELLIDOL. Trade name for diacetylamino-azotoluene.

PELLITORY RESIN *v.* RESINS.

PELLOTINE *v.* MEZCALINE.

PENNETTIER'S GREEN. *Hydrated chromium sesquioxide v.* CHROMIUM.

PENNYROYAL, OIL OF, *v.* OILS, ESSENTIAL.

PENTACONTANE, $C_{50}H_{102}$, a member of the paraffin series, has been observed to occur in Lancashire coal, as a brittle dark brown, wax-like substance, sparingly soluble in organic solvents in the cold, but soluble in benzene, toluene and carbon tetrachloride on heating. When purified it forms a white amorphous solid, m.p. 93·0°, b.p. 420°–422°/15 mm. Sp.gr. 0·9422 when solid, 0·7940 when liquid at 93° (Sinnatt and Barash).

PENTADECATOIC ACID $C_{14}H_{29}COOH$, m.p. 51°, b.p. 257° (100 mm.), is obtained by the oxidation of methylpentadecylketone (Krafft, Ber. 1879, 1671) and by heating pentadecyl alcohol with potassium carbonate (Panics, Monatsh. 15, 14).

PENTAHYDROXYBENZENE *v.* PHENOL AND ITS HOMOLOGUES.

PENTAL *v.* SYNTHETIC DRUGS.

Cyclo-**PENTANEDIONE** *v.* KETONES.

Cyclo-**PENTANONE** *v.* KETONES.

PENTLANDITE. A sulphide of nickel and iron, (Fe,Ni)S, crystallised in the cubic system. Crystals are not known, but there is an octahedral cleavage or parting. The mineral forms granular aggregates or veins in other sulphide ores, and has a pale bronze-yellow colour with metallic lustre. The streak is pale bronze-brown. Sp.gr. 4·6–5·0; H. 3½–4. It often occurs intimately intermixed with pyrrhotite, and is not readily recognised except on polished and etched surfaces of the ore. It is, however, distinguished by its octahedral cleavage and non-magnetic character (pyrrhotite being slightly magnetic); further, pentlandite soon weathers to a brassy-yellow colour, then showing up against the darker bronze-coloured pyrrhotite. It is probable that the nickel of most niccoliferous pyrrhotite ores is present as pentlandite. In the separation of these minerals by a magnetic process fine grinding is essential.

Analysis I is of pentlandite from Lillehammer, Norway (T. Scheerer, 1843). II, Beiern, Nordland, Norway (J. H. L. Vogt, 1892). III, Sudbury, Ontario (S. L. Penfield, 1893). IV, Sudbury (C. W. Dickson, 1903). V, Eas a' Chosain (Essochossan) Glen, 1 mile W.S.W. of Inveraray, Argyllshire (D. Forbes, 1868). VI, Creag-an-Iubhair (Craigmure), 10½ miles S.W. of Inveraray (D. Forbes, 1868); also As 0·04.

	I.	II.	III.	IV.	V.	VI.
Ni .	21·07	32·97	34·23	39·85	11·17	10·01
Co .	—	0·45	0·85	trace	trace	1·02
Fe .	40·21	30·51	30·25	25·81	49·97	50·87
Cu .	1·78	0·28	—	—	trace	trace
S .	36·64	34·15	33·42	34·35	37·50	37·99
Insol.	—	0·29	0·67	—	1·20	0·38
	99·70	98·65	99·42	100·15	99·84	100·31

The mineral has been detected in niccoliferous pyrrhotite and copper-pyrites ores occurring in connection with norite rocks at several places in Norway, and in the important deposits of a similar character in the Sudbury district in Ontario. Cleavage surfaces of pentlandite over an inch across are met with in the Creighton mine, and the Worthington mine, but in many of the mines of the Sudbury district the mineral, though presumably present, is not visible. It has also been found in pyrrhotite at the Alexo nickel mine in northern Ontario. (A. P. Coleman, The Nickel Industry, with special reference to the Sudbury region, Ontario, Dept. Mines, Ottawa, 1913.) Other localities of ores of this kind in which pentlandite has been detected are: Friday mine in San Diego Co., California; Prospect Hill, Litchfield, Connecticut; Gap mine, Lancaster Co., Pennsylvania; Insizwe Range in East Griqualand, South Africa; Sohland in Saxony. (C. F. Tolman and A. F. Rogers, A Study of Magmatic Sulfid Ores, Stanford University, California, 1916.) The mineral from the nickel mines, which were formerly worked on a small scale, near Inveraray in Argyllshire has been called *Inverarite*. Analyses V and VI with low nickel correspond with 5FeS·NiS, and were, perhaps, made on material still intermixed with pyrrhotite. A related mineral containing up to 38 p.c. Ni from Heazlewood in Tasmania has been called *Heazlewoodite*. L. J. S.

PENTOSANS, PENTOSES *v.* CARBOHYDRATES.

PEONIDIN, PEONIN *v.* ANTHOCYANINS.

PEPERINO *v.* TUFF.

PEPPER is the dried fruit of *Piper nigrum* (Linn.), a plant of the same family, *Piperaceæ*, as the Betel pepper and Long pepper.

It is a climbing plant, from 12 to 20 ft. high, growing in the East and West Indies and cultivated in many tropical countries. The fruit is borne on terminal flower stalks, 20 to 30 on each stem, the berries being about 5 mm. in diameter. It is gathered when it begins to turn red, dried in the sun or by artificial heat, after which it becomes black and shrivelled. Two crops are collected annually.

For method of cultivation in Sarawak (now gradually dying out owing to the spread of a disease among the berries called by the Chinese 'Voo Choon'), *see* Notes on Sarawak Trade, Journal of the Roy. Soc. of Arts, July 28, 1922, in which an account is given of the method of making black and white pepper as practised in the Upper Sarawak district and at Lundu

and Simatau, and in the Batang Lupar, and Rejang districts.

The chief varieties coming into the market at the present time are Mangalore (very little), Malabar, Ceylon, Java, and Tellicherry, Trang, Penang, and Singapore, the first mentioned being the most esteemed in the trade.

Preparation.—Black pepper is the whole berry gathered in the green condition and dried in the sun or in the case of some varieties, as that of Singapore, over a fire.

White pepper is the same berry, gathered when more mature, but deprived of a portion of the pericarp or outer skin by macerating in water, drying, and then rubbing between the hands, from 6 to 12 p.c. of husks being thus obtained. The berries even after this are larger than those of Black pepper, but in no other respect does the greater degree of ripeness show itself.

Composition.—The constituents to which the flavour and aroma of pepper are due are a resin, an alkaloid, *piperine*, and a volatile oil. According to W. Johnstone, *piperidine* is also present, but this has been contradicted (Zeitsch. öffentl. Chem. 1904, 10, 137). The usual plant constituents, including much starch, make up the bulk of the material.

The following table shows the comparative composition of the two varieties.

TABLE I.

COMPOSITION OF PEPPER.

(Richardson, U.S. Dept. of Agriculture, Bureau of Chem. Bul. 13, II. 206.)

	Black pepper	White pepper
Water . . .	8·0 to 11·0	8·0 to 11·0
Ash	2·75 ,, 5·0	1·0 ,, 2·0
Volatile oil . .	0·50 ,, 1·75	0·5 ,, 1·75
Piperine and resin	7·0 ,, 8·0	7·0 ,, 8·0
Starch . . .	32·0 ,, 38·0	40·0 ,, 44·0
Crude fibre . .	8·0 ,, 11·0	4·11 ,, 8·0
Albuminoids .	7·0 ,, 12·0	8·0 ,, 10·0

Pepper itself is mainly employed as a condiment, the shells being used for tinned foods, sausages, etc. Black pepper is *official* in the British Pharmacopœia, and like the volatile oil acts as a carminative and stomachic.

Adulteration.—The number of different substances which have been recorded from time to time as adulterants of pepper is very large, but in this country but little sophistication has been detected of recent years.

Excessive proportions of mineral matters may be present, owing to the whole berries having been insufficiently cleansed from adherent earth; or to their having been coated with kaolin, French chalk, or similar material, so as to enable black pepper to counterfeit the white variety; a high ash may also result from the deliberate addition of mineral substances to the ground pepper.

The commonest adulterant, however, is added starch, that of rice being most frequently employed. Some years back, ground olive stones ('poivrette' or 'pepperette') were frequently met with in samples examined under the Food and Drugs Acts, and many prosecutions resulted. The husk removed from white pepper in the course of manufacture is frequently added to both black and white peppers, being in the latter case bleached. In white pepper it must certainly be regarded as an adulterant if the proportion of added husk is at all substantial, and numerous successful prosecutions have been recorded. The addition of long pepper (*Piper longum*) was formerly fairly common.

A more objectionable offence arises from the craze for whiteness in pepper, and it is hardly too much to say that, but for this, adulteration would be much less frequent. White pepper is bleached to make it whiter still, and fetches a higher price in consequence although very deficient in aroma. The exact process is kept secret, though it is believed to involve the use of bleaching powder or sulphurous acid. The bleaching process naturally removes much of the aroma and the purchaser pays a higher price for an impoverished product, which is much more likely to become mouldy in consequence of the treatment it has undergone.

According to Parry (Chem. and Druggist, 1914, 84, 34) white pepper is sometimes tinted with minute quantities of turmeric.

Of the rarer adulterants which, however, still appear to be met with in America and elsewhere, may be mentioned spent ginger, mustard hulls, linseed meal, ground almond shells, sawdust and barium sulphate.

Troccoti and Verona-Rinati (Zeit. f. Unter. Nahr. u. Genussm. 1912, 24, 736) record the presence amongst whole peppercorns of the seeds of *Rhamnus Cathartiens* (Buckthorn), and of *Schinas Motte* (so-called American or false pepper).

Detection of adulteration.—(1) Microscopical examination. For the detection of added starch the ground sample should be examined in water or dilute glycerol without attempting to reduce the material to a very fine powder. The masses of starch granules, cemented together with protein substances, will then retain the form of the cells in which they were enclosed.

Comparatively few isolated starch grains will be seen in this case if the sample consists of pepper only, but foreign starches will be easily visible. Rice starch alone presents any difficulty owing to its small size and general resemblance to pepper starch. The granules of the latter vary from 0·5 to 5μ in diameter, are polygonal or round and show a distinct hilum under a high power. Those of rice, of similar shape, vary from 2 to 10μ in diameter and are also collected in aggregates which are never entirely broken up, and when the sample is examined in polarised light are easily picked out in the dark field from amongst the pepper masses by their much more brilliant appearance.

In examining microscopically for olive stones and for excess of pepper husk it is of advantage to obtain the coarser and heavier particles and examine them separately. This may be done by sifting through a 40 or 50 mesh seive, by sedimentation in chloroform, or by removal of the starch by boiling with dilute hydrochloric acid. The structure of the particles may be rendered more easily visible by digesting for 2 or 3 days in chloral hydrate or by treatment with dilute nitric acid and potassium chlorate.

The most conspicuous structural elements of the outer shell are the spiral vessels and the

hypodermal stone cells of the pericarp, distinguished from the stone cells of the endocarp (beaker cells) by their larger and more variable size (15μ to 20μ and sometimes 100μ long), less regular shape, thicker walls and yellow-brown colour. The polygonal beaker cells have pitted walls and are colourless.

In examining white pepper for added shell, care must be taken to see that the above-mentioned structures of the outer layer are present in substantial proportion. The inner layer is a normal constituent of white pepper, and may be found in considerable quantities in the cheaper grades, where its presence is regarded by the trade as legitimate, although the addition of the dietetically much more valuable outer pericarp is looked upon as an adulteration.

With polarised light, ground olive stones are easily recognised as they stand out brightly in the dark field, and exhibit a reddish tint. Most of the structural elements of pepper remain almost dark, but long pepper exhibits a bluish tinge under these conditions.

Various methods of staining have been suggested which will render the presence of 'poivrette' visible to the naked eye, but they are used to greater advantage in conjunction with the microscope. Dilute caustic soda colours olive stones, and also bleached pepper husks bright yellow while pepper remains unchanged. A solution of aniline in strong acetic acid leaves pepper unaltered, but turns ground olive stones or almond shells yellow brown.

Mixed with a few drops of freshly made 1 p.c. solution of phloroglucinol in alcohol and a drop of concentrated hydrochloric acid added olive stones, almond shells and substances containing much lignified tissue are stained pale to dark red, while pepper is only slightly altered to the naked eye. (For other reactions, *see* Analyst, xx. 1895, 181.)

Chemical analysis.—For the routine chemical examination, the ash and the ash insoluble in HCl should be first estimated, the analyst being guided as to further determinations by the results of the microscopic examination.

If the total ash exceeds 5·5 in the case of black pepper or 3 in the case of white pepper, added mineral matter may be suspected, and a more detailed analysis is required. The composition of the ash of pepper is as follows:—

TABLE II.

ASH OF PEPPER.

(Rottger, Arch. f. Hygiene, 1886, Bd. IV. 183, and Blythe.)

No. of samples	Black pepper 4. Per cent.	White pepper 2. Average.
K_2O . . .	24·4 to 34·7	6·13
Na_2O . . .	1·5 ,, 5·5	0·79
CaO . . .	11·6 ,, 16·1	33·09
MgO . . .	3·3 ,, 13·0	10·59
Fe_2O_3 . . .	0·3 ,, 2·2	2·04
MnO_2 . . .	0·19 ,, 0·8	0·55
P_2O_5 . . .	8·5 ,, 11·1	30·05
SO_3	4·0 ,, 9·6	3·50
Cl	5·4 ,, 8·5	0·72
Silica or sand .	1·5 ,, 6·5	2·05
CO_2	14·0 ,, 20·0	10·96

The amount of foreign starch can only be arrived at indirectly by calculation from the proportion of fibre, or pentosans, or fixed ether extract. On account of the somewhat wide variations in the composition of genuine pepper, no single determination affords trustworthy evidence.

If ground olive stones, almond shell, or similar substances have been detected, the most useful determinations are those of the fibre and starch. The starch should be determined by the diastase method after previous extraction with alcohol and ether, or by Ewer's method (J. Inst. Brewing, 1898, 552). The fibre by boiling 2 grms. of the sample under an inverted condenser with 200 c.c. of 1·25 p.c. sulphuric acid, and, after filtering and washing, extracting for a like period with the same volume of 1·25 p.c. soda, the fibre being finally filtered, dried, and weighed on a tared filter or Gooch crucible. The ash should be deducted. (For a quick method, which, however, gives different results from the above, *see* Stokes, Analyst, 12, 14.) If the fibre in a white pepper much exceeds 5 p.c. and microscopical examination shows the presence of the outer portions of the shell, the excess of husk may be taken as roughly equal to the percentage of fibre less 5 multiplied by 3.

For special purposes, the estimation of the piperine may be required and should be carried out as follows:—

The dried alcoholic extract from 50 grms. of the sample is treated with caustic alkali to dissolve resins, etc., well washed on a filter with the same solution, then with water; the precipitate is next dissolved in alcohol, the latter evaporated and the residue redissolved in a small volume of alcohol, the piperine precipitated by the addition of water and collected on a tared filter, washed, dried, and weighed.

In the case of non-nitrogenous adulterants, the proportion of nitrogen affords a useful basis for calculation, as the nitrogen, other than that present in the piperine, is fairly constant in amount in genuine peppers. It is best, therefore, to determine total nitrogen by the Arnold-Gunning method (*i.e.* mixing 1 grm. of the sample with about the same weight of copper sulphate and red oxide of mercury and digesting with sulphuric acid and potassium sulphate in the usual manner for the ordinary Kjeldahl process). The nitrogen in the ether extract should then be determined in the same manner and deducted from the total nitrogen. The nitrogen figure for the ether extract, multiplied by 20·36, gives a rough measure of the piperine.

Turmeric in proportion too small to give the boric acid reaction may be detected under the microscope by staining with a reagent made by mixing 1 grm. of diphenylamine with 30 c.c. of 90 p.c. alcohol, and 25 c.c. of sulphuric acid when the turmeric particles assume a fine purple colour. Bill's test (Parry, *l.c.*).

The tables on page 91 show the results of the analysis of pepper and of some of the most likely organic adulterants.

Black pepper should be free from added pepper shells, pepper dust, and other pepper by-products.

TABLE III.

Results of analyses of various varieties of Black and White pepper and of pepper shells by Winton, Ogden, and Mitchell; Winton and Bailey (An. Rep. Connect. Exp. Station 1898, 198–199; 1903, 158–164); and by Doolittle, Mich. Dairy and Food Dept., Bull. 34.

No. of samples	Black pepper 65			White pepper 35			Pepper shells 7	
	Max.	Min.	Average	Max.	Min.	Average	Max.	Min.
Moisture	12·95	8·09	10·26	14·47	8·04	10·90	11·01	7·00
Ash, total	8·04 [1]	3·09	5·02	4·28	0·86	1·71	28·81	7·82
Ash, insoluble in HCl	2·59 [1]	0·0	0·61	0·86	0·0	0·17	22·90	0·79
Ash, soluble in water	3·32	1·65	2·52	1·16	0·12	0·38	4·66	1·53
Starch (Diastase method)	41·75	22·05	35·64	63·60	48·88	54·97	15·30	2·30
Ether extract, volatile	2·20	0·65	1·29	0·95	0·49	1·04	1·11	0·68
,, ,, non-volatile	10·44	6·60	7·90	7·94	5·65	6·58	4·97	1·51
Fibre	18·89	10·05	11·88	7·65	0·10	3·87	32·15	21·06
Nitrogen, total	2·53	1·86	2·15	2·14	1·85	1·99	2·36	1·72
Nitrogen in fixed ether extract	0·45	0·25	0·32	0·34	0·24	0·30	0·15	0·20
	in 20 samples			in 10 samples			in 3 samples	
Alcohol extract	11·86	8·31	9·44	8·55	7·19	7·66	6·30	4·00

TABLE IV.

Analysis of pepper adulterants. (Campbell Brown, Analyst, 1887, 12, 24.)

——	Ash	Starch	Fibre	Soluble in boiling dilute acid	Soluble in dilute alkali
White poivrette	1·33	none	48·48	38·32	14·08
Black ,,	2·47	none	47·69	34 55	17·66
Ground almond shells	2·05	none	51·68	23·53	24·79
Ground olive stones	1·61	none	45·38	39·08	15·04

Standards. The United States standards for pepper are as follows :—

	Black pepper	White pepper
	Not to exceed	
Ash	7·0 p.c.	4·0 p.c.
Ash insol. in hydrochloric acid	2·0 ,,	0·5 ,,
Fibre	15·0 ,,	5·0 ,,
	not less than	
Starch	25·0 ,,	50·0 ,,
Fixed ether extract	6·0 ,,	6·0 ,,
Percentage of N. in fixed ether extract	4·0 ,,	3·25 ,,

Long Pepper is the fruit of *Piper officinarum* [(Miq.) C.DC.] and *P. longum* (Linn.) (N. O. *Piperaceæ*) which grows in the islands of the Malay archipelago, Bengal, and the Philippine islands.

The fruit spike has the form of catkins from 2 to 6 cm. long and 4 to 7 mm. wide in the case of *P. officinarum*, that of *P. longum* being shorter and broader. It consists of numerous minute berries disposed along and partly embedded in an elongated axis. It has an odour and flavour somewhat resembling ordinary pepper but weaker and less agreeable, the smell becoming decidedly objectionable on warming.

It contains about the same amount of volatile oil and about half the amount of piperine present in ordinary pepper, and owing to the fact that the fruit often trails on the ground the ash is liable to be high, owing to the inclusion of clay and sand from the adherent soil, to remove which no special steps are taken. The figures obtained by the analyses of five samples by Campbell Brown and by Winton, Ogden, and Mitchell, are as follows :—

	Max.	Min.
Total ash	9·61 p.c.	8·10 p.c.
Ash insol. HCl	0·22 ,,	0·15 ,,
Ether extract	7·24 ,,	4·90 ,,
Starch and matters convertible into sugar	49·34 ,,	42·88 ,,
Fibre	15·70 ,,	5·76 ,,
Nitrogen	2·30 ,,	2·00 ,,
Alcohol extract	8·67	
Starch by diastase	39·55	

It does not come into the retail market, and its chief use is in the pickling and canning trade, and, formerly, at all events, for the adulteration of black and white pepper (*q.v.*), for which purpose it may be bleached.

It has been used medicinally as a stimulant and carminative. C. H. C.

PEPPER, CAYENNE. Cayenne pepper is the dried and powdered fruit of various small fruited species of *Capsicum* of which *C. fastigiatum* (Blume) and *C. frutescens* (Linn.) are the most important. The plant is indigenous in tropical America and is cultivated in hot and temperate climates in many parts of the world.

The fruit is elongated, conical, and has a shiny, bright red surface becoming dull red and shrivelled when dry. The pods are from ½ to 2 cm. long and contain numerous yellowish,

[1] These figures, obtained from Achein pepper, which often contains hollow kernels and shell in excess, were only approached in one other sample of the same kind. Apart from these the maximum figures would be—Ash 7·00 p.c. and insoluble ash 1·80 p.c.

flattened kidney-shaped seeds, 3 to 4 mm. in diameter.

Paprika, a large fruited variety of *Capsicum annuum*, is grown in Hungary, Spain, Italy, France, and Turkey. The fruit is from 2 to 5 cm. long and has a bright red or yellow shiny surface, but has not the intensely hot and pungent flavour of cayenne pepper. It is used chiefly on the Continent.

Other varieties of *C. annuum* are also widely employed on the Continent and in America for pickling.

Pimiento is a large fruited pepper of bright red colour and very mild flavour, used for stuffing olives and as colouring matter.

Composition. The characteristic constituents are a red colouring matter, present only in the pod, soluble in ether, light petroleum, carbon disulphide, or chloroform, and an active principle *capsaicine*, $C_{18}H_{28}NO_3$, to which the characteristic flavour is mainly due, and which, though it preponderates in the pod, is also found in the seed (Micko, Zeitsch. Nahr. Genussm. 1, 818; 2, 411). There is also a tasteless and odourless fixed oil and an oleoresin (*syn. capsican*), which, as used in medicine, is a mixture of fat, resin, and various other substances extracted by the solvent employed (Alcohol, B.P. Codex; Acetone, U.S. Pharmacopœia). Analyses by Richardson (U.S. Depart. of Agric., Div. of Chem. Bull. 13, 1887) of *Capsicum annuum* yielded the following results:

TABLE I.

	Seed	Pod	Fruit
Loss at 100°C. . .	8·12	14·75	11·94
Albuminoids (N×6·25)	18·31	10·69	13·88
Fat (ether extract) .	28·54	5·48	15·26
Fibre . . .	17·50	23·73	21·09
Ash	3·2	6·62	5·20

Cayenne pepper is mainly used as a condiment and also in canary and chicken foods. The whole fruit, ripe or unripe, appears in the market as capsicums or chillies, low grade fruits of large size being usually employed under these names for pickling, etc. The dried fruit of *Capsicum minimum* is 'official' in the British Pharmacopœia. Taken internally, it acts as a stomachic and carminative to the alimentary canal, externally as an irritant and vesicant.

Adulteration. Although a long list of adulterants is given in most text-books, cayenne pepper is rarely sophisticated in this country at the present time. The addition of foreign starches, such as wheat and rice, of mineral substances, gypsum and red ochre and, to mask the presence of light-coloured adulterants like starch and gypsum, such diverse materials as turmeric, ground redwood, and aniline dyes should still be looked for. Ground nutshells and olive stones have also been found comparatively recently.

Detection of adulteration. Microscopical examination will suffice to detect the adulterants of vegetable origin. The presence of foreign starches will be at once apparent. The very minute starch grains of cayenne pepper are only present in very small numbers, the quantity being dependent on the ripeness of the fruit when gathered, and are usually embedded in cells.

The microscopical appearance of cayenne pepper is very characteristic and comparison with a standard sample will enable any of the above-mentioned vegetable adulterants to be detected with comparative ease (*v.* PEPPER).

Preparations of the sample, both before and after removal of the fat, should be mounted in water or dilute glycerol. Fragments of the epicarp showing quadrilateral cells of which the walls have a slightly wavy outline, but are not beaded, and which are arranged in rows, serve to distinguish cayenne pepper from paprika. (For further details as to the structural differences between different species of capsicums, *see* Pharm. J. 1901, 13, 552; 1902, 69, 3; or Winton, Microscopy of Vegetable Foods.)

The presence of mineral adulterants will be indicated by a high ash; nutshells or olive stones will raise the proportion of fibre (estimated as in PEPPER, *q.v.*). For the detection of oil, soluble vegetable or coal tar colours, the ether extract of the sample may be shaken with a mixture of 2 parts of carbon disulphide and 15 parts of ethyl alcohol. The carbon disulphide will dissolve the oil and the natural colouring matter of the capsicum, while most aniline colours will pass into the supernatant alcohol layer.

Table II. (Parry, Food and Drugs) shows the limits within which the figures obtained by the analyses of cayenne pepper are found to vary, and Table III. gives figures for chillies and Table IV. for paprika.

TABLE II.

	Maximum	Minimum
Moisture . . .	7·5	3·5
Ether extract, volatile .	2·8	0·7
,, ,, non-volatile	15·5	19·0
Alcohol extract . .	30·0	25·0
Starch by diastase method	1·5	0·8
Fibre	25·0	20·0
Nitrogen . . .	2·40	2·08
Ash, total . . .	7·2	5·0
,, soluble in water .	3·3	0·30
,, insol. in HCl . .	0·3	0·05

TABLE III.

Analyses of whole chillies. (Zanzibar, Japan and Bombay. 8 samples in all.) (Winton, Ogden and Mitchell, Ann. Report, Connecticut, Exper. Station, 1898, 200.)

—	Maximum	Minimum	Average
Moisture . . .	7·08	3·67	5·73
Ether extract, volatile .	2·57	0·73	1·35
,, ,, non-volatile	21·81	17·17	20·15
Alcohol extract . .	27·61	21·52	24·35
Starch (diastase method)	1·46	0·80	1·01
Fibre	24·91	20·35	22·35
Nitrogen, total . .	2·34	2·13	2·18
Ash, total . . .	5·96	5·08	5·43
,, soluble in water .	4·93	3·30	3·98
,, insol. in HCl . .	0·23	0·05	0·15

Analysis of paprika (whole pods). (Doolittle and Ogden, J. Amer. Chem. Soc. 30, 1908, 1481.)

TABLE IV.

	Maximum	Minimum	Average
Loss of 100°C.	9·39	7·26	8·52
Ether extract, volatile	1·25	0·17	0·93
,, ,, non-volatile	11·99	7·42	9·57
,, ,, ,,			
Iodine number	136·8	130·3	133·5
Reducing matters (acid conversion) as starch	21·4	16·52	19·46
Fibre	19·83	15·1	15·33
N×6·25	17·44	14·06	15·51
Ash total	7·06	5·24	6·22
,, soluble in water	5·79	4·59	5·14
,, insol. HCl	0·22	0·05	0·08
Alkalinity of ash, total	8·00	6·10	7·04
,, ,, sol. in water	5·70	4·07	4·93

Analyses by Tolman and Mitchell (U.S. Dept. of Agric. Bureau of Chemistry, Bulletin No. 163, 1913) of Hungarian paprika (a variety of *Capsicum annuum*) are shown in Table V.

Standards. The official standard of the U.S. Department of Agriculture for cayenne pepper provides that it shall be the dried ripe fruit of *C. frutescens*, *C. baccatum*, or any small fruited species of capsicum, and that the fixed ether extract should not be below 15 p.c., the total ash not more than 6·5 p.c., the ash insoluble in HCl not more than 0·5 p.c., starch (diastase method) not more than 1·5 p.c., and fibre not more than 28 p.c.

The capsicum of the B.P. is the dried fruit of *Capsicum minimum* (Roxb.), and should not yield more than 7 p.c. of ash (B.P. 1914). C. H. C.

PEPPERMINT. The *Mentha piperita* (Linn.) (U.S.P.; not B.P.) of Europe and America; *M. arvensis* (Linn.) of Japan. Extensively grown for the sake of its volatile oil, which is procured by distilling its leaves. At Mitcham about 1½ tons of the fresh herb are loaded into the still for a charge, the distillation of which takes about 7 hours. The condensed water and oil is run into a separator with a perforated plate at the top, and the floating oil is drawn whilst the 'mother-liquor' is used over again. From 7 to 10 lbs. of oil is the average yield from

TABLE V.

	Shells, seeds, placentæ and stems		Shells, seeds and placentæ		Seeds and placentæ		Shells.		Stems.	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Loss at 70°C. *in vacuo*	3·29	3·76	3·11	4·16	3·73	4·23	3·44	4·00	4·66	5·78
Total ash	5·08	6·03	4·66	5·56	3·38	3·80	6·29	7·11	9·84	11·35
Ash insol. HCl	0·24	0·33	0·20	0·31	0·21	0·30	0·22	0·37	0·66	1·20
Fixed ether extract	12·21	16·43	13·94	17·35	25·97	27·56	5·14	6·90	2·11	3·05
Crude Fibre	20·69	22·76	20·47	23·18	20·89	21·60	22·20	24·07	29·34	32·86

1½ tons of herb. The oil and the preparations made from it are used as aromatics, carminatives, and stimulants, and are useful in medicine for griping pains. It is also employed in the form of mint-camphor, or menthol, for outward application in affections of the nerves (*v.* OILS, ESSENTIAL).

The following colour reaction serves to differentiate quickly the Japanese oil derived from *Mentha arvenis* from the oil of *M. piperita*:—Five drops of the oil and 1 c.c. of glacial acetic acid are heated with one drop of nitric acid in a water-bath to about 60° C. for about two minutes. In the case of the oil of *M. piperita* a violet or bluish colour develops in a few minutes, with a copper-coloured fluorescence by reflected light. Japanese oils usually show a straw colour or sometimes a very faint blue colour, but no copper-coloured fluorescence. The method of storage of *M. piperita* oils has some effect on the reaction, oils stored in open vessels in sunlight giving a negative result after a few months; but in every case the oils recover this property on being treated with nascent hydrogen, and subsequently steam distilled. Japanese oils treated in the same way still give a negative result. E. O. Eaton (Journ. Assoc. Off. Agric. Chem. 1922, 5, 597).

Oil of peppermint amounts on the average to 0·8 of the total plant used. The crystals of peppermint camphor are obtained from the distillate by cooling; the oil having been drained off, the process is repeated, when a tolerably pure oil is secured. After a third repetition no crystallisation takes place.

Menthol $C_{10}H_{19}\cdot OH$ or peppermint-camphor, in its commercial state is a white crystallised mass, melting at about 35° and boiling at 210°. When purified by distillation the melting-point is raised to 42° and the boiling-point to 212°, $[\alpha]_D = -50°$ in 10 p.c. alcoholic solution.

Menthone $C_{10}H_{18}O$ is a colourless mobile liquid, b.p. 207°, and the ketone corresponding to menthol, from which it can be obtained by careful oxidation, and into which it is convertible by reduction with sodium in ethereal solution. This reduction may be applied with advantage to peppermint oil residues containing a mixture of menthone and menthol. Theoretically 4 optically active menthones and 8 menthols are possible; a mixture of (some of) these is produced by the reduction of thymol with nickel and hydrogen (Pickard and Littlebury, Trans. Chem. Soc. 1912, 101, 109).

Menthene $C_{10}H_{18}$ is produced in the dehydration of menthol by various reagents, and is a colourless liquid, b.p. 165° (*v. Peppermint camphor*, art. CAMPHORS *v.* TERPENES). G. B.

PEPPERMINT CAMPHOR *v.* CAMPHORS.

PEPPERMINT OIL *v.* OILS, ESSENTIAL.

PEPSIN. *Pepsinum* (B.P.; U.S.P.; *Pepsine*, Fr.; *Pepsin*, Ger.). Pepsin is a ferment or

enzyme, existing in the acid secretion of the mucous membrane of the stomach or gastric juice. It possesses the property, in presence of dilute acid, and, within certain limits of temperature, of converting albuminous food into soluble peptone. Schwann (Müller's Arch. 1836) made the first attempt to prepare the ferment in a form available for supplying artificial digestion in cases where the natural function was imperfectly performed. To obtain a good product and to preserve it requires great care and skill. The animals generally selected are the hog, sheep, and calf, and the preparation often employed is simply the dried mucous membrane of the stomach. A glycerine extract of the mucous membrane may be precipitated with alcohol. Aqueous extracts may be precipitated with sodium chloride, dialysed and evaporated *in vacuô* below 40°. For preparation of purest pepsin *v.* Nencki and Sieber (Zeitsch. physiol. Chem. 1901, 32, 291); Pekelharing (*ibid.* 1902, 35, 8); Schrumpf (Beit. chem. Physiol. Path. 1905, 6, 396).

Pepsin of commerce varies much in activity (Grierson, Year-Book, Pharm. 1887, 263). 5 milligrams digested with 12·5 grams of coagulated and firm white of fresh eggs and 125 c.c. of acidified water containing about 0·2 p.c. of hydrogen chloride at 40·5° for 6 hours with frequent shaking should give an almost clear solution, containing only a few small flakes. This method of testing, which is adopted by the British Pharmacopœia, is the outcome of numerous investigations as to the effect of different temperatures and different forms of albumen, together with the selection of an acid and determination of its appropriate strength. The U.S.P. process is similar, but with digestion for 2½ hours at 52°. Compare E. Schütz (Arch. f. d. ges. Physiol. 1900, 80, 470); J. Schütz (Zeitsch. physiol. Chem. 30, 1). Within certain limits the quantity of protein digested is proportional to the square root of the pepsin concentration (E. Schütz, Zeitsch. physiol. Chem. 1885, 9, 577).

In addition to the method given above, various other methods have been devised for the determination of peptic activity (Meunier, J. Pharm. Chim. [iv.] 14, 555; Kuttner, Zeitsch. physiol. Chem. 52, 63; Fuld and Levison, Biochem. Zeitsch. 6, 473; Einhorn, Chem. Zentr. 1908, ii. 1295; Brewster, J. Biol. Chem. 1921, 46, 119).

On the question of the identity of pepsin and rennin, *see* Hammarsten (Zeitsch. physiol. Chem. 1918, 102, 33, 105), Gewin (*ibid.* 54, 32), Ringer (Arch. Néeland physiol. 1918, 2, 571), Taylor (J. Biol. Chem. 5, 399); Fenger (Journ. Amer. Chem. Soc. 1923, 45, 249). G. B.

PEPTAMINES *v.* PITUITARY BODY.

PERBORAX. Sodium perborate

$$NaBO_3,4H_2O$$

v. BORON. According to Foerster the composition of this salt is $NaBO_2{\cdot}H_2O_2,3H_2O$ (Zeitsch. angew. Chem. 1921, 34, 354).

PERCARBONATES $M_2C_2O_6$ may be prepared by electrolysing a strong solution of the normal carbonates at −30° to −40° (Riesenfeld and Reinhold, Ber. 1909, 42, 4377). The potassium salt is a bluish-white, amorphous deliquescent powder which decomposes on heating into potassium carbonate, carbon dioxide and oxygen, and is a strong oxidising and bleaching agent. When added to a neutral solution of potassium iodide, it immediately liberates iodine, thus:

$$K_2C_2O_6+2KI=2K_2CO_3+I_2$$

no oxygen being evolved. The above authors regard this action as characteristic for the percarbonates, and therefore maintain that the 'percarbonates,' such as Na_2CO_4, obtained by the action of hydrogen peroxide on sodium carbonate (Tanatar, Ber. 1899, 32, 1544; J. Russ. Phys. Chem. Soc. 1902, 34, 952), are additive compounds of carbonates and hydrogen peroxide This contention is, however, denied by Tanatar (Ber. 1910, 43, 127, 2149; *see* also Wolffenstein, *ibid.* 639; Riesenfeld, *ibid.* 566, 2594).

According to Riesenfeld and Mau (Ber. 1911, 44, 3589) the true percarbonates can be distinguished from carbonates containing hydrogen peroxide of crystallisation by the fact that the former give a quantitative liberation of iodine from a neutral solution of potassium iodide, whereas the latter liberate practically no iodine.

The only percarbonates which have been prepared are those of the alkali metals, and of barium (Wolffenstein and Peltner, Ber. 1908, 41, 271). (*Cf.* Riesenfeld and Mau, Ber. 1911, 44, 3595.) Sodium hydrogen percarbonate

$$4Na_2CO_2,H_2CO_4$$

has been used as a disinfectant and in the preparation of hydrogen peroxide (D. R. P. 188569).

PEREIRO BARK of the Brazilian tree *Geissospermum vellosii*, is used locally as a febrifuge, and contains three alkaloids, *geissospermine* $C_{19}H_{24}O_2N_2,H_2O$, *pereirine* $C_{19}H_{24}ON_2$(?) (Hesse, Annalen, 1880, 202, 141), and *vellosine* $C_{23}H_{28}O_4N_2$ (Freund and Favet, *ibid.* 1894, 282, 247). The first of these is crystalline and yields a crystalline sulphate; the lethal dose for frogs is 2 mg.; for guinea pigs 10 mg. The second is amorphous and yields amorphous salts. The third is crystalline, m.p. 189°; it contains two hydrogen atoms more than brucine, which it also resembles somewhat in physiological action, and in containing two methoxy groups. Vellosine is a monacid, tertiary base and very poisonous (Schultze, Annalen, 1894, 282, 266). G. B.

PEREZONE (*Pipitzahoic acid*) $C_{15}H_{20}O_3$, a crystalline compound of an orange colour, melting at 103°–105°, contained in the root, 'raiz del Pipitzahuac,' of a plant, *Perezia adnata*, found in Mexico and used as a purgative (Weld, Annalen, 1885, 95, 188; Anschütz and Leather, Ber. 1885, 18, 709; 1886, 49, 709; Mylius, Ber. 1885, 18, 936; Remfry, Chem. Soc. Trans. 1913, 103, 1076).

Perezone forms salts $C_{15}H_{19}O_3M$, due to the presence of a phenolic group. Has also the properties of a quinone; is readily reduced to a colourless substance which is quickly reoxidised in air; and yields with aniline and other amines, amino derivatives which are hydrolysed by boiling with dilute acids, yielding *hydroxyperezone* $C_{15}H_{20}O_4$. On treatment with sulphuric acid this substance yields *perezinone* $C_{15}H_{18}O_3$.

Perezone heated to 210°–270° yields a sublimate of *pipitzol* $C_{15}H_{20}O_3$, a colourless, crystalline substance isomeric with perezone, optically active ($[\alpha]_D+13{\cdot}1°$); insoluble in water; soluble in alcohol, ether, benzene, or acetone; does not react with aniline, hydroxylamine or phenyl-

hydrazine, or bromine in chloroform solution. M.p. 140°–141°. It yields a crystalline monoacetyl derivative, *acetyl pipitzol*

$$C_{15}H_{19}O_3{\cdot}CO{\cdot}CH_3$$

m.p. 114°–115° (corr.) $[\alpha]_D$+6·2. *Benzoylpipitzol* $C_{15}H_{19}O_3{\cdot}COPh$. Colourless prisms from light petroleum; m.p. 154°–155° (corr.).

For evidence of the constitutional formulæ of hydroxyperezone, perezinone, and perezone, *see* Fichter, Jetzer, and Leepin (Annalen, 1913, 395, 15); Remfry (*l.c.*).

PERFUMES (SYNTHETIC). Prior to 1875 perfumes were prepared almost entirely from plants by various processes of distillation and extraction (*v.* OILS, ESSENTIAL); musk and civet, used from the very earliest times, were of animal origin; synthethic perfumes were unknown. To-day, almost every flower-perfume may be imitated by a so-called 'synthetic oil,' the odour of which closely resembles that of the natural product. The faithfulness of the imitation varies very much with the different scents; it is doubtful, for instance, whether any purely synthetic violet or rose oil at present in existence can vie with the natural fragrance. The term 'synthetic' thus applied is misleading: the 'synthetic oils' are in fact mixtures of a number of chemical compounds, some of which have been obtained by synthetic processes, others merely isolated from the essential oils in which they occur. In many cases, the most satisfactory results are only obtained by blending the 'synthetic' with a natural oil. Thus, jasmine oil is added with good effect to the 'synthetic' oils of rose, lilac, muguet, &c.; the ketone (jasmone) characteristic of jasmine oil has been isolated, but its composition has not as yet been determined, and no synthetic substance hitherto obtained is entirely satisfactory in replacing it. In certain cases where the constitution of the characteristic constituent of a particular perfume has not been elucidated, the substitute may consist of a substance possessing an entirely different structure from that of the natural product yet closely resembling it in smell. Thus the characteristic principle of musk is a non-nitrogenous ketone of unknown constitution: synthetic musk consists, however, of various di- or trinitro-derivatives of tertiary butyl toluene.

The synthetic perfume industry may be said to have originated with the manufacture of vanillin from eugenol, described in a patent taken out by Tiemann in 1876 (Eng. Pat. 1611); shortly afterwards in 1879, coumarin and heliotropin were prepared, and since that time the production of synthetic substances for use in the blending of perfumes has steadily continued.

Not only is the scent of an oil modified by the presence of minute traces of odoriferous substances, but the degree of dilution is an important factor in producing the requisite odour. The solvent most commonly used is a 95–96 p.c. ethyl alcohol. The condition of the alcohol is of great importance; it must be free from fusel oil; and taste, smell, and colour must give no indication of impurities. Methyl alcohol finds little application, largely owing to the fact that the commercial alcohol contains more or less acetone, which has an injurious effect. 95 p.c. alcohol is also used for preparing the infusions of the flower pomades, 1250 kilos. of solvent being used to extract 1000 kilos. of pomade. The extraction is twice repeated so that three infusions are obtained, diminishing in strength. For the cheaper sorts of extracts and toilet-waters, the rectified spirits of wine is replaced by potato spirit.

The least soluble of the synthetic perfumes are the artificial musks, of which less than 1 p.c. dissolves in alcohol. Benzyl benzoate and benzyl cinnamate are used as solvents for these, 1 kg. of the former dissolving 500 grams ketone moschus or 250 grams Musc Baur.

The extracts which are sold as handkerchief perfumes are known as quadruple, triple, double, and simple, according to their strength; 12 parts of a triple extract will furnish 20 parts of double or 30 parts of simple extract by dilution with alcohol and water; in the preparation of the double and simple extracts, the second infusions of the flower pomades are also utilised.

For the preparation of aqueous and dilute alcoholic toilet waters, only a limited number of substances are available, owing to the sparing solubility of the majority of perfumes in water. The most soluble are phenyl ethyl alcohol (2 p.c.), benzyl alcohol (1 p.c.) and vanillin (0·8 p.c.).

Relation between constitution and smell.—(*v.* Odour and Chemical Constitution).

The list of substances, used in the compounding of perfumes is a long one. The most important of these are as follows:

Hydrocarbons. With the exception of styrene and *p*-cymene, the hydrocarbons which occur in the natural perfumes and contribute to their odour belong chiefly to the terpene group. Diphenyl methane (*q.v.*) is used in synthetic geranium oil. Pinene, with its characteristic odour of pine-needles, is the chief constituent of pine-needle oil; *d*-limonene occurs in the oils of lemon, orange, orange-flower, bergamot, &c.: menthene is found in oil of peppermint and carvene in caraway oil (*v.* TERPENES). The halogen derivatives and *α*-chloro-and *α*-bromostyrolene are used in the preparation of oil of hyacinth.

Alcohols. The saturated fatty alcohols occur commonly as esters; the alcohols of the terpene and of the aromatic series are either free or in combination with fatty acids. The latter are used in preparing, amongst others, the oils of rose, jasmine, hyacinth and lilac.

OLEFINIC TERPENE ALCOHOLS.

Citronellol $C_{10}H_{20}O$

$CH_2{:}C(CH_3)CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}CH_2OH$

$(CH_3)_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}CH_2OH$

b.p. [*d*-citronellol] (17 mm.) 117°–118°; sp.gr. 0·8565 at 17·5°; $[\alpha]_D$+4° at 17·5°; n_D 1·45679; b.p. [*l*-citronellol] (15 mm.) 113°–114°; sp.gr. 0·8612 at 20°; $[\alpha]_D$−4° 20′; n_D 1·45789 (Tiemann and Schmidt, Ber. 1896, 29, 906).

d-Citronellol occurs in geranium and in Java citronella oils; *l*-citronellol has been isolated from geranium and from rose-oils. Prolonged discussion has taken place as to the identity of citronellol with the alcohols, 'rhodinol,' 'reuniol,' and 'roseol' isolated from geranium or rose-oil. It is now accepted that the last two are mixtures of citronellol with geraniol. The difference between *l*-rhodinol and *d*-citronellol does not depend only on optical *iso*merism; they differ structurally in the position of the double

bond. Rhodinol contains the grouping $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C$; whereas in citronellol the structure $\begin{matrix}CH_3\\CH_2\end{matrix}\!\gg\!C$ is present (Barbier and Bouveault, Compt. rend. 1897, 124, 1308). Barbier and Locquin (Compt. rend. 1913, 157, 1114) succeeded in converting *d*-citronellol into *d*-rhodinol by treating the acetate with hydrogen bromide in acetic acid solution; the bromhydrin is heated with sodium acetate for one hour at 160° and on saponification *d*-rhodinol and $\gamma\eta$-dimethyloctane-$\alpha\eta$-diol are obtained. The perfume of the synthetic *d*-rhodinol is entirely similar to that of the naturally occurring *l*-rhodinol. The most satisfactory explanation of the discrepant results obtaned by earlier observers appears to be that offered by Harries and Himmelmann (Ber. 1908, 41, 2187), who, from studying the action of ozone on the citronella compounds, arrived at the conclusion that citronellol consists of a mixture of two isomerides, differing in the position of the double bond as represented above. By the action of ozone on citronellol, 20 p.c. of acetone is produced corresponding to 20 p.c. of the rhodinol structure $(CH_3)_2C{=}C\!<$. The evidence for the formula of citronellol is based chiefly upon the behaviour of the corresponding aldehyde, citronellal (*v. infra*).

Citronellol occurs in company with geraniol: the boiling-points of both alcohols lie very close to each other, but geraniol is the less stable and may be destroyed by heating with phthalic anhydride at 200° or with benzoyl chloride at 140°–160° (Barbier and Bouveault, Compt. rend. 1896, 121, 530). Citronellol may be obtained from citronella oil by reducing with sodium amalgam and acetic acid when the aldehydes citral and citronellal are reduced to citronellol. The mixture of geraniol and citronellol is then treated with phosphorus trichloride in ethereal solution at a low temperature: a phosphite of citronellol is formed which is extracted by water, geranyl chloride remaining in the ethereal layer (Tiemann, Ber. 1896, 29, 921).

Cold dilute $KMnO_4$ oxidises citronellol to a polyhydric alcohol, converted by chromic acid mixture to acetone and β-methyl adipic acid. It is characterised by a liquid phthalic acid ester giving a crystalline silver salt, and by its oxidation to citronellal, the latter being identified by its semi-carbazone (m.p. 84°) or its compound with β-naphthocinchoninic acid.

The isomeric alcohols of the formula $C_{10}H_{18}O$, *linalool*, *geraniol*, and *nerol*, readily undergo mutual transformation. Thus if geraniol be heated at 200° with water in an autoclave, linalool is formed (Schimmel Report, April, 1898, 25). When treated with hydrochloric acid, geraniol is converted into linalyl chloride, from which linalool may be obtained by the action of alcoholic potash or of a solution of silver nitrate (Tiemann, Ber. 1898, 31, 832; 1895, 28, 2138). On the other hand, by the action of acetic anhydride on linalool, a mixture of the acetates of geraniol, nerol, and terpineol is formed (Tiemann and Schmidt, Ber. 1895, 28, 2137; Tiemann and Semmler, *ibid.* 1893, 26, 2714; Stephan, J. pr. Chem. 1898, [ii.] 58, 109; Zeitschel, Ber. 1906, 39, 1780). They frequently occur together and have all three been detected in the oils of rose, neroli, petit-grain and linaloe.

Linalool $C_{10}H_{18}O$

$(CH_3)_2C:CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3)(OH)CH:CH_2$ or $CH_2:C(CH_3)CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3)(OH)CH:CH_2$ b.p. 198°–199° (13 mm.) 88·3°–89·5°; sp.gr. 0·870 at 15°, $n_D^{20°}$ 1·4668 (Gildmeister, Arch. Pharm. 1895, 233, 179); *l*-linalool $[\alpha]_D$ −20° 7′ : *d*-linalool $[\alpha]_D$ +19° 8′ (Stephan).

Linalool is the chief constituent of linaloe oil; it occurs as the *l* form in the oil from Cayenne, and both as *d* and *l* forms in that from Mexico. Amongst other oils in which it has been detected are coriander (*d*), sweet orange (*d*), nutmeg (*d*), ylang-ylang (*l*), rose (*l*), reunion geranium (*l*), petit-grain (*l*), bergamot (*l*), neroli (*l*), lemon (*l*); in the four last of these and in lavender and jasmine-flower oils, it is also present as the acetate; the butyrate occurs in lavender oil and the *iso*butyrate in Ceylon cinnamon oil and the *iso*valerate in the oil of sassafras leaves. It is isolated by fractional distillation and purified by the action of phthalic anhydride on its sodium compound; sodium linalyl phthalate is soluble in water and after saponifying with alcoholic potash, the linalool may be extracted with ether. Citral is obtained by oxidation with chromic acid mixture (Bertram and Waldbaum, J. pr. Chem. 1892, [ii.] 45, 599).

Dilute $KMnO_4$ in the cold oxidises it to polyhydric alcohols, which are converted by chromic acid mixture into acetone and lævulic acid (Tiemann and Semmler, Ber. 1895, 28, 2130); by reduction with nickel and hydrogen, 2 : 6-dimethyl octane has been obtained (Ber. 1908, 41, 2083).

It may be identified by its phenyl urethane (m.p. 65°–66°) or its α-naphthyl urethane (m.p. 53°) or it may be oxidised to citral.

Geraniol $C_{10}H_{18}O$

$(CH_3)_2C:CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3):CH{\cdot}CH_2OH$

b.p. (17 mm.) 120·5°–122·5°; sp.gr. 0·8894 at 20°; $n_D^{20°}$ 1·4766 (Tiemann and Semmler, Ber. 1893, 26, 2711).

Geraniol forms the chief constituent of Palmarosa and of German and Turkish rose oils and occurs in geranium, citronella, lemongrass, and many other oils. It is also found as acetate, *iso*valerate, *n*-caproate, and tiglate. It is isolated by fractional distillation and purified either by means of its crystalline compound with calcium chloride (Bertram and Gildmeister, J. pr. Chem. 1896, [ii.] 53, 233; 1897, 56, 507), or by treating its sodium compound with phthalic anhydride in benzene solution (Tiemann and Krüger, Ber. 1896, 29, 1901). By oxidation with chromic acid mixture, citral is obtained (Tiemann, Ber. 1898, 31, 828), from which geraniol may again be obtained by reduction. The catalytic action of copper at a high temperature has also been utilised for the oxidation of geraniol to citral (Bouveault, Bull. Soc. chim. 1908, [iv.] 3, 119). The action of chromic acid mixture after treating with $KMnO_4$, produces acetone, lævulic, and oxalic acids (Semmler, Ber. 1893, 26, 2720). Geraniol is more stable than linalool to the action of acids and is quantitatively converted by acetic anhydride into geranyl acetate. By the action of dilute H_2SO_4, terpin hydrate is obtained (Tiemann

and Schmidt, *ibid.* 1895, 28, 2138): concentrated formic acid reacts forming α-terpineol, terpinene, and dipentene (Bertram and Gildmeister, J. pr. Chem. 1894, [ii.] 49, 195; Stephan, *ibid.* 1899, [ii.] 60, 244). The phthalic acid ester (m.p. 47°), the α-naphthyl urethane (m.p. 47°–48°), and the di-phenyl urethane (m.p. 124°) are characteristic.

Nerol $C_{10}H_{18}O$, stereoisomeric with geraniol; b.p. 226°–227°: 125° (25 mm.); sp.gr. 0·8813 at 15°; occurs in neroli-oil, chiefly as acetate (Hesse and Zeitschel, J. pr. Chem. 1902, [ii.] 66, 502), in rose, linaloe, and petit-grain oils, and in the oil of *Helichrysum angustifolium* (Heine & Co., D. R. P. 209382). It may be obtained by the action of acetic anhydride on linalool (Zeitschel, Ber. 1906, 39, 1780): about 5 p.c. is formed on reducing citral. It has a rose-like smell and in chemical behaviour resembles geraniol. Nerol does not, however, give a crystalline compound with $CaCl_2$ and reacts with dilute H_2SO_2, forming terpin hydrate more readily than does geraniol. Its di-phenyl urethane melts at 52°–53°.

SESQUITERPENE ALCOHOL.

Farnesol $C_{15}H_{26}O$

$(CH_3)_2C:CH\cdot CH_2\cdot CH_2\cdot C(CH_3):CH\cdot CH_2\cdot CH_2\cdot C(CH_3):CH\cdot CH_2OH$

b.p. (10 mm.) 160°; sp.gr. 0·885 at 18°; $n_D^{20°}$ 1·4899; occurs in lily of the valley, lilac, acacia, rose, mignonette flower, and musk seed oils. In the latter, 0·12 p.c. of farnesol is present; it is isolated by extracting the seeds with ether, and saponifying the extracted material with alkali. By repeated treatment with ether, a crude oil is obtained, from which farnesol can be isolated as its phthalic ester. It is unaltered on keeping for a long time, and can best be identified by converting it into the semi-carbazone of the corresponding aldehyde (m.p. 133°–135°); oxidation with chromic acid gives a 50 p.c. yield of the aldehyde farnesal (Kerschbaum, Ber. 1913, 46, 1732). Farnesal oxime was converted into the nitrate of farnesenic acid: on treating this with alcoholic caustic soda solution, farnesenic acid (b.p. (16 mm.) 202°–206°), acetic acid, and dihydropseudo ionone were obtained. The structure of the latter was shown to be

$(CH_3)_2C:CH\cdot CH_2\cdot CH_2\cdot C(CH_3):CH\cdot CH_2CH_2COCH_3$

The constitution ascribed to farnesol was confirmed by Harries and Haarman (Ber. 1913, 46, 1737), who investigated the products found on decomposing its ozonides. Pure farnesol is almost odourless; if a very dilute alcoholic solution be allowed to evaporate, after some time an intensely sweet smell reminiscent of lily of the valley is noticed; Kerschbaum suggests that this may be due to an oxidation product formed slowly by the action of the air. Hitherto farnesol has not given very successful results in the hands of the perfumer; possibly this may be owing to insufficient dilution.

CYCLIC TERPENE ALCOHOLS.

Terpineol *v.* TERPENES.
Borneol *v.* CAMPHORS.
iso-**Borneol** *v.* CAMPHORS.

AROMATIC ALCOHOLS.

Benzyl alcohol $C_6H_5\cdot CH_2OH$; b.p. 205°, sp.gr. 1·05 at 15°, $n_D^{20°}$ 1·540; occurs free in tuberose, ylang ylang, carnation, jasmine oils, &c., as acetate in ylang ylang, hyacinth, and jasmine oils, as benzoate (ylang ylang), cinnamate salicylate (ylang ylang), and phenyl acetate (neroli). It is manufactured by the action of lead oxide at 100° or of potassium carbonate on benzyl chloride, or by the action of potassium acetate and saponification of the acetate formed. It is characterised by a phenyl urethane (m.p. 78°), a phthalic acid ester (m.p. 106°–107°), and a semi-carbazone of its pyroracemic ester (m.p. 176°).

Phenyl ethyl alcohol $C_6H_5\cdot CH_2\cdot CH_2OH$; b.p. 220°–222° (740 mm.), sp.gr. 1·0235 at 15°, $n_D^{20°}$ 1·53212; occurs in rose and neroli oils as benzoate and phenyl acetate. In preparing rose-oil by steam distillation, much of the phenyl ethyl alcohol is lost. It is obtained by reducing (1) phenyl acetaldehyde with sodium amalgam, and (2) phenyl acetic ester with sodium and alcohol; in its manufacture other methods are probably used. It is purified by means of its compound with calcium chloride (Bouveault and Blanc, D. R. P. 164294; Compt. rend. 1903, 136, 1676; 1903, 137, 60). It may be separated from citronellol and geraniol by its greater solubility in dilute alcohol. The phenyl urethane melts at 80°, the phthalic acid ester at 188°–189°.

Phenyl propyl alcohol $C_6H_5\cdot CH_2\cdot CH_2\cdot CH_2OH$; b.p. 235°, sp.gr. 1·007 at 15°. This alcohol, hyacinth-like in odour, is obtained by reducing cinnamic ester with sodium and alcohol (Schimmel, D. R. P. 116091) or by reducing benzyl aceto-acetic ester (Bouveault and Blanc, D. R. P. 164294). The phenyl urethane melts at 47°–48°.

Cinnamic alcohol (*v.* CINNAMIC ALCOHOL) is characterised by a hyacinth-like odour.

ESTERS.

The methods used in the preparation of the esters are (1) the action of hydrochloric acid on a mixture of alcohol and acid; (2) the action of the alcohol or its sodium compound on the fatty acid anhydride or chloride, the reaction on the large scale being carried out in pyridine solution.

In preparing the esters of those olefinic terpene alcohols which themselves undergo change on heating with acid reagents, a mixture of the alcohol and acid may be treated with small quantities of a mineral acid below 30° (Bertram, D. R. P. 80711).

A large number of patents deal with the preparation of the esters of the cyclic terpene alcohols: thus in preparing *iso*borneol esters, camphene and the fatty acid may be heated with P_2O_5 (Schindelmeiser, D. R. P. 229190), pinene hydrochloride warmed with the fatty acid, and anhydrous zinc sulphate (D. R. P. 196017), &c.

The fatty acid esters find wide application as fruit essences. A list of those more especially used in perfumery is appended.

Ester	Boiling-point	Synthetic oil in which used
Bornyl formate	90° (10 mm.)	Lime blossom
Citronellyl „ .	97°–100° (10 mm.)	Geranium
Geranyl „ .	119°–121° (15 mm.)	„
Amyl acetate	112° (760) 38° (12 mm.)	
Benzyl „	262° (760)	Jasmine
Bornyl „	98° (10 mm.)	
Geranyl „	128°–129° (16 mm.)	Rose
Linalyl „	97° (10 mm.)	Bergamot
Phenyl ethyl „		Orange flower
Terpineol „	110°–115° (10 mm.)	Bergamot, Lilac
Geranyl propionate . . .		Bergamot
Geranyl butyrate		Geranium
Geranyl caproate		„
Ethyl œnanthylate		
Ethyl pelargonate		

Amongst the aromatic acids esters used are :

Ester	Boiling-point	Synthetic oil in which used
Methyl benzoate	199·2° (746 mm.)	Ylang-ylang, hyacinth
Ethyl „	211°–212° (729 mm.)	Ylang-ylang
Benzyl „	323°–324°	Largely used as a solvent for non-alcoholic perfumes, *e.g.* artificial musks
Phenyl ethyl „		Hyacinth
Linalyl „		Ylang-ylang
Methyl salicylate	217° (730 mm.)	Oil of wintergreen
Ethyl „	234° (743 mm.)	
Amyl „	276°–277° (743 mm.)	Clover

Isobutyl phenyl acetate and other esters of this acid have also proved of use.

The esters of the unsaturated and ketonic fatty acids also find considerable application. The $\alpha\beta$-unsaturated acids, *e.g.* nonylenic acid, may be prepared by condensing aldehydes with malonic acid in pyridine solution (Weizmann and Harding, Chem. Soc. Trans. 1901, 97, 299).

Esters of tiglic acid occur in geranium oil (Schimmel, Report, Oct. 1913); the following esters have been prepared by condensing the alcohol with tiglic acid chloride in benzene solution in the presence of pyridine; geranyl tiglate, b.p. (7 mm.) 149°, sp.gr. 0·9279 at 15°; citronellyl tiglate, b.p. (7 mm.) 144°, sp.gr. 0·9090 at 15°; phenyl ethyl tiglate, b.p. (7 mm.) 139°, sp.gr. 1·0257 at 15°.

The acetylene carboxylic acids are prepared by acting on the sodium compounds of the acetylene hydrocarbons with CO_2 in ethereal solution. Heptine (C_7H_{12}) and octine (C_8H_{14}) are thus converted to *octinic* and *noninic* acids; on boiling these with alcoholic caustic potash, esters of β-ketonic acids are obtained (Moureu, D. R. PP. 132802, 1902; 133631; 158252, 1905).

These esters are also directly prepared by treating the sodium compounds of the hydrocarbons with chloroformic ester in ethereal solution.

PHENOLS AND THEIR ETHERS.

***iso*Eugenol** (*v.* EUGENOL).
Anethole (*v.* ANETHOLE).
Thymol (*v.* PHENOL AND ITS HOMOLOGUES).
Naphthol (*v.* NAPHTHALENE).

The methyl and ethyl β-naphthyl ethers are both known as nerolin, the former as yara-yara, the latter as bromelia. In very dilute solution the odour resembles that of orange-flower.

ALDEHYDES.

General methods used for the production of higher fatty aldehydes are—

(1) The reduction of the ester of the corresponding acid to the alcohol and subsequent oxidation of the alcohol, heated copper being used as the catalytic agent.

(2) The method of Darzens (D. R. PP. 174239, 174279), by which a ketone is condensed with chloracetic ester in the presence of an alkaline condensing agent; on heating the glycidic acid thus obtained, CO_2 is evolved and the aldehyde formed. A large number of aldehydes have been produced by this method.

$$(CH_3)_2CO + ClCH_2\cdot COOEt \rightarrow (CH_3)_2C\underset{\backslash\,/}{-}CH\cdot COOEt$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O$$
$$(CH_3)_2C\cdot CHCOOH = (CH_3)_2CH\cdot CHO + CO_2$$
$$\quad\backslash\,/$$
$$\quad O$$

(3) A mixture of formic with a higher fatty acid is passed over titanium oxide heated to 250°–300° (Sabatier and Mailhe, Compt. rend. 1912, 154, 56).

(4) Distillation of the barium salt of the corresponding acid with barium formate *in vacuô* [Schimmel, D. R. P. (1902) 126736].

Higher fatty aldehydes have been detected in oils of rose, lemon, &c.

***n*-Octaldehyde** $C_8H_{16}O$; b.p. 60°–63° (10 mm.), sp.gr. 0·827 at 15°, n_D 1·41955. Prepared from octyl alcohol (Schimmel, Rep. 1899, 25). The β-naphthyl cinchoninic acid derivative melts at 234°.

***n*-Nonaldehyde** $C_9H_{18}O$; b.p. 80°–82° (13 mm.), sp.gr. 0·8277 at 15°, $n_D^{16°}$ 1·42452. First detected in rose-oil (Schimmel, Rep. 1900, 53) and subsequently in orris, cinnamon, mandarin, and lemon oils.

A yield of 71 p.c. is obtained by distilling α-hydroxydecoic acid (Bagard, Bull. Soc. chim. 1907, iv. 346; Bouveault and Blanc, Compt. rend. 136, 1903, 167). Identified by the oxime (m.p. 69°), semi-carbazone (m.p. 100°); yields pelargonic acid (b.p. 252°) on oxidation.

***n*-Decaldehyde** $C_{10}H_{20}O$, b.p. 93°–94° (12 mm.), 207°–209° (755 mm.), sp.gr. 0·828 at 15°, $n_D^{15°}$ 1·42977 (Stephan, J. pr. Chem. 1900, [ii.] 62, 525). Occurs in orris, neroli, mandarin and other oils. A yield of 52 p.c. is obtained by distilling α-hydroxyundecylic acid. The oxime melts at 69°, semi-carbazone at 102°, β-naphthocinchoninic acid compound at 237°.

Of recent years there has been a growing tendency to recognise the value of the higher aldehydes of the acetic series in synthetic perfumery, and several of the best known artificial orange and rose perfumes contain traces of these aldehydes. Nonaldehyde is used in the manufacture of cyclamen, muguet, lilac, and artificial rose; octaldehyde in jasmine, jonquil, hyacinth, and narcissus. French perfumers use duodecyl aldehyde in making the finest artificial violet perfumes; the addition of from 5–10 p.c. of this aldehyde to any of the bodies of the

ionone type produces a bouquet far superior to that of simple ionone (J. Soc. Chem. Ind. 1911, 1279).

OLEFINIC TERPENE ALDEHYDES.

Citral (geranial) $C_{10}H_{16}O$

(*a*) $(CH_3)_2C:CH\cdot CH_2\cdot CH_2\cdot C(CH_3):CH\cdot CHO$
(*b*) $CH_2:C(CH_3)CH_2\cdot CH_2\cdot CH_2\cdot C(CH_3):CH\cdot CHO$

b.p. 110°–112° (12 mm.); sp.gr. 0·8972 at 15°, n_D 1·4931. Occurs in lemon grass, citronellol, rose, and many other oils, as two stereoisomeric forms (*a*) and (*b*) (chiefly as the former), giving semi-carbazones melting respectively at 164° and 171° (Tiemann, Ber. 1899, 32, 115). On oxidising geraniol with chromic acid mixture, a 30–40 p.c. yield of citral is obtained, and it is also formed when linalool and nerol are oxidised. It has been synthesised by distilling a mixture of the calcium salts of geranic and formic acids. On heating with acids, it is converted into cymene (Tiemann, Ber. 1899, 32, 107); with caustic soda, methyl heptenone and acetaldehyde are formed. Oxidation with chromic acid mixture converts it into methyl heptenone, but if first oxidised with cold permanganate and then with chromic acid, acetone and lævulic acid result. In acetic acid solution, it is reduced by sodium amalgam to geraniol. The action of sodium bisulphite produces different compounds according to conditions. (Tiemann, *ibid.* 1889, 31, 3317.) The normal compound from which the citral may again be regenerated by the action of alkalis, is formed in the presence of a small quantity of sulphurous acid. The β-naphtho-cinchoninic acid compound (m.p. 200°) is used for its identification.

Skita has shown that citronellal and citronellol are formed by reduction in presence of palladium. The condensation with acetone is described under Ionone.

Citronellal $C_{10}H_{18}O$

$(CH_3)_2C:CH\cdot CH_2\cdot CH_2\cdot CH(CH_3)CH_2\cdot CHO$
$CH_2:C(CH_3)CH_2\cdot CH_2\cdot CH_2\cdot CH(CH_3)CH_2\cdot CHO$

b.p. 205°–208°, 103°–105° (25 mm.); sp.gr. 0·8538 at 17·5°, n_D 1·4481, α_D 12° 30′. Occurs chiefly in citronella oil. It is reduced by sodium amalgam to citronellol; the action of acids results in closing the ring, *iso*pulegol being formed. The action of sodium bisulphite has been studied by Tiemann (Ber. 1898, 31, 3305). By adjusting the conditions, methods of separating citral and citronellal have been devised. Thus whilst citral reacts with dilute solutions of sodium bisulphite and bicarbonate, citronellal reacts only with concentrated solutions (Ber. 1899, 32, 815). Much discussion has taken place as to the identity of natural citronellal with the compound obtained by oxidising rose-oil citronellol, the latter compound being designated by Barbier and Bouveault as rhodinal. The conversion of rhodinal to menthone under the influence of acids is affirmed by Barbier and Bouveault (Compt. rend. 1896, 122, 737; 1904, 138, 1699; Bull. Soc. chim. 1900, [iii.] 23, 458), although denied by Tiemann and Schmidt (Ber. 1897, 30, 38).

Harries and Himmelmann (Ber. 1908, 41, 2187) have since shown that in citronellal the two isomeric compounds formulated above are present. The semi-carbazone (m.p. 82·5°) and β-naphthyl cinchoninic acid compound (m.p. 225°) are characteristic. Prins (Chem. Weekblad, 1917, 14, 692) claims to have isolated the isomerides corresponding to the two formulæ given above from citronellal, by repeated fractionation. To the compound, b.p. 198°–200°, sp.gr. at 14°, 0·8745 with a semi-carbazone, m.p. 82·5°–83°, the first of the above formulæ is ascribed; the substance, b.p. 203°–204°, sp.gr. at 14°, 0·880 with a semi-carbazone, m.p. 85°–86°, is represented by the second formula.

AROMATIC ALDEHYDES.

Benzaldehyde $C_6H_5\cdot CHO$ (*v* BENZALDEHYDE).

Phenyl acetaldehyde $C_6H_5\cdot CH_2\cdot CHO$; b.p. 75° (5 mm.), sp.gr. 1·0315 at 15°, $n_D^{20°}$ 1·52536 (Schimmel and Co.). This may be obtained from phenyl chlor (or α-brom) lactic acid or from phenyl and α-brom-styrol. By gentle oxidising agents it is converted into the corresponding acid. It is unstable and tends to polymerise on keeping.

Cinnamaldehyde $C_6H_5\cdot CH:CH\cdot CHO$ (*v.* CINNAMIC ALDEHYDE).

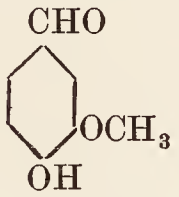
Salicyaldehyde $C_6H_4(OH)CHO$ (*v.* SALICYLIC ALDEHYDE).

Anisaldehyde $C_6H_4(OCH_3)CHO$, *p*-methoxy benzaldehyde (Aubépine); b.p. 248° (corr.), 91° (4 mm.), sp.gr. 1·126–1·129 at 15°, $n_D^{20°}$ 1·572. Prepared by the oxidation of anise oil, consisting chiefly of anethole



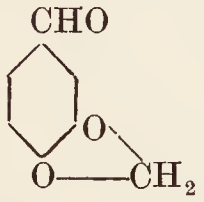
with about 10 p.c. of the isomeric estragole. The oxidising agents used are dilute nitric acid, chromic acid mixture or ozone. It is also obtained by the methylation of *p*-hydroxybenzaldehyde. The semi-carbazone melts at 203°–204°, the two modifications of the oxime at 63° and 132° respectively.

Vanillin



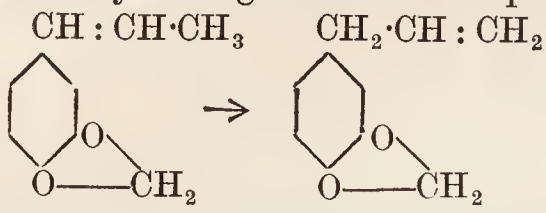
(*v.* VANILLIN.)

Heliotropin (Piperonal)



methylene protocatechuic aldehyde. White crystals, m.p. 36°; b.p. 236°. Heliotropin has the characteristic odour of heliotrope flowers, but it has only been detected with certainty in the flowers of *Spiræa ulmaria* (Linn.). It was originally synthesised by Fittig and Mielk from piperonylic acid, and was prepared from piperine. Ground pepper is mixed with slaked lime and water, evaporated to dryness and extracted with ether. The residue is boiled with alcoholic potash and the potassium piperate formed oxidised with permanganate. From the filtered solution, heliotropin crystallises out. It is now manufactured by the oxidation of *iso*safrol with permanganate or chromic acid. The product is steam distilled, extracted with ether and purified by means of its bisulphite compound. The yield produced by oxidation of safrole is

much less, so that the safrole is converted first to *iso*safrole by boiling with alcoholic potash.



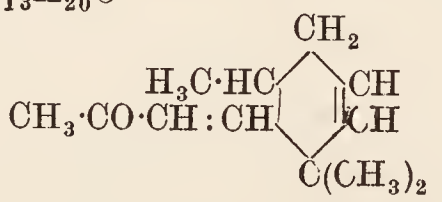
The use of ozone as oxidising agent gives a good yield of a pure product (Otto). It may also be prepared by the action of methylene iodide on protocatechuic aldehyde in presence of alkali.

Since its introduction in 1879, the price has fallen from £150 to 30*s*. per kilo. It must be kept in a cool, dark place, since it becomes gradually discoloured on exposure to light; in the hot weather it is conveniently kept in alcoholic solution. It may be identified by a semi-carbazone (m.p. 224°–225°), by reduction to piperonyl alcohol (m.p. 51°), or by oxidation to piperonylic acid (m.p. 228°).

KETONES.

The most important members of this class are irone, the odoriferous principle of orris-root ionone, the basis of the synthetic violet perfumes. Jasmone, the ketone isolated by Hesse from jasmine oil, the constitution of which is as yet unknown, and muscone, the ketone of unknown constitution isolated from musk, cannot yet be included amongst the synthetic perfumes.

Irone $C_{13}H_{20}O$

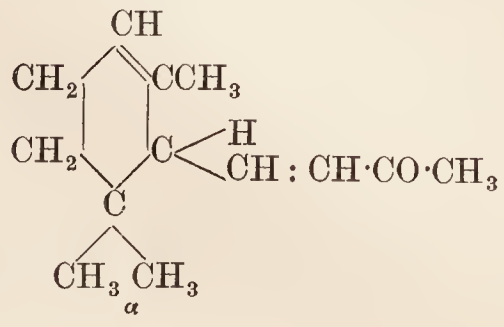


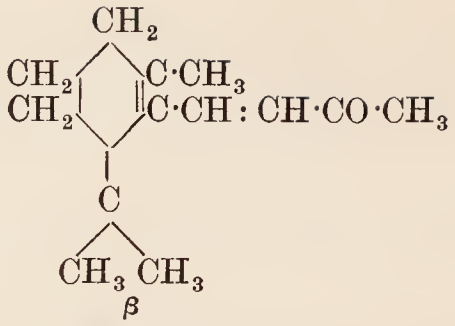
b.p. 144° (16 mm.); sp.gr. 0·939 at 20°, $[\alpha]_D$ +40°, n_D 1·50113 (Tiemann and Krüger).

The orris root is extracted with ether and the extracted matter distilled in steam. The volatile fraction contains irone, myristic, and oleic acids and their esters and oleic aldehyde. The acids and esters are removed by treating with alcoholic potash, the aldehydes oxidised by means of silver oxide, and finally the irone separated by conversion into its phenyl hydrazone (Tiemann and Krüger, Ber. 1893, 26, 2675). It may be obtained more conveniently from orris-root oil by fractional distillation. The smell of the pure substance is sharp when concentrated, but if largely diluted, resembles that of violets. Its synthesis has been accomplished by Merling and Welde (Annalen, 1909, 366, 119) who, starting from *iso*propylidene acetoacetic ester, succeeded in obtaining Δ-4-*cyclo*citral; on condensing this with acetone, irone was produced.

It is characterised by a *p*-bromophenyl hydrazone (m.p. 174°–175°), and an oxime (m.p. 121·5°), crystallising with difficulty.

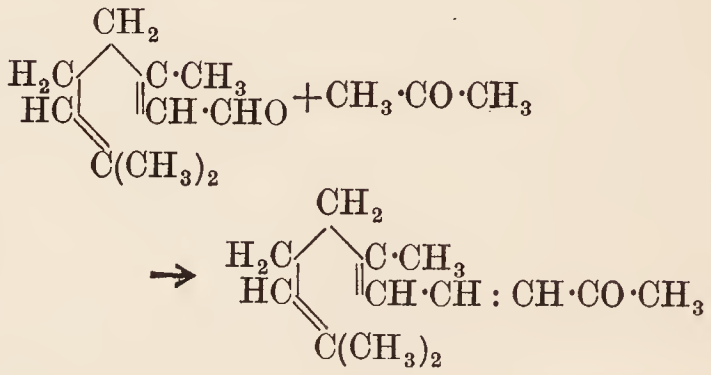
Ionone $C_{13}H_{20}O$





α-Ionone, b.p. 123°–124° (11 mm.), sp.gr. 0·932 at 20°, n_D 1·4980; β-Ionone, b.p. 127°–128·5° (10 mm.), sp.gr. 0·946 at 17°, $n_D^{17°}$ 1·521.

Ionone, obtained by Tiemann and Krüger (Ber. 1893, 26, 2691) in an unsuccessful endeavour to synthesise irone, forms the basis of synthetic violet perfumes. Citral and acetone interact, in the presence of alkaline condensing agents, forming *pseudo*-ionone, a pale yellow strongly refractive oil, boiling at 143°–145° (12 mm.).



This, when treated with acids, is converted into a mixture of the isomeric cyclic ketones α- and β- ionone. As the alkaline condensing agent dilute baryta water may be used, or the dry mixture of citral and acetone may be shaken with dry sodium peroxide (Kayse, D. R. P. 127661), or with PbO, LaO, or borates (Haarman and Reimer, D. R. P. 130457). The proportion of α- or β- compound produced depends on the nature of the acid chosen to effect the closing of the ring. Concentrated sulphuric acid, or the prolonged action of dilute acids produces chiefly the β- compounds, concentrated phosphoric or formic acids almost entirely the α- derivative. α-Ionone is transformed by concentrated sulphuric acid into the β- compound. Various methods have been devised for the separation of the α- and β- forms. If the mixed bisulphite compounds be distilled in steam, β- ionone distils over; the α- compound remains behind in combination and is liberated on the addition of alkali. The difference in solubility of the semi-carbazones may also be utilised.

α-Ionone is characterised by a *p*-bromphenyl hydrazone (m.p. 142°–143°).

β-Ionone is characterised by a *p*-bromphenyl hydrazone (m.p. 116°–118°).

The semi-carbazones melt respectively at 107°–108° (α) and 148° (β).

A large number of patents deal with the preparation of similar products. Homologues of acetone and other ketones may replace acetone (Fr. Pat. 269884). Ivalderine is thus produced by condensing with methyl ethyl ketone, ianthone with methyl pentenone (Fr. Pat. 278333), ganthone with mesityloxide (D. R. P. 118288). Calcium chloride and iron chloride have also been used as condensing agents. The characteristic violet odour of these

compounds only becomes apparent in dilute solutions.

Ionone hydrate and its homologues prepared by condensing citral hydrate with acetone are also described (Coulin, D. R. PP. 198483, 200654).

LACTONE.

Coumarin (*v.* COUMARIN) has the scent characteristic of new mown hay.

OXIDE.

Cineol (*v.* CAMPHORS).

COMPOUNDS CONTAINING NITROGEN.

Indole, a constituent of jasmine-flower oil (*v.* INDOLES).

Scatole occurs in civet (*v.* INDOLES).

Methyl anthranilate, m.p. 24°–25°; b.p. 132° (14 mm.), sp.gr. 1·168 at 15°. Occurs in neroli, tuberose, ylang-ylang, jasmine flower, bergamot and other oils. It consists of white crystals which show a blue fluorescence; solutions are also fluorescent.

Methyl methylanthranilate, m.p. 18·5°–19·5°; b.p. 130° (13 mm.), sp.gr. 1·120 at 15°. Occurs in mandarin oil.

Nitrobenzene is used as a substitute for bitter almond oil.

Trinitro-tert.-butyltoluene

$$(NO_2)_3C_6H(CH_3)C(CH_3)_3$$

(Tonquinol or Musc Baur), pale yellow crystals (m.p. 96°–97°). Prepared by condensing *iso*butyl chloride with toluene in the presence of $AlCl_3$ and nitrating the product formed; during the process, the *iso*butyl is transformed to tertiary butyl. The butyl toluene is added to 5 times its weight of a mixture of 1 part HNO_3 (1·5) and 2 parts fuming H_2SO_4 containing 15 p.c. anhydride and heated at 100° for 8–9 hours.

THE USE OF SYNTHETIC SUBSTANCES IN THE BLENDING OF PERFUMES.

By suitably mixing and diluting the compounds enumerated above, a great variety of perfumes may be produced and many of the natural oils and extracts imitated. The exact composition of these substitutes varies with the particular maker and is kept as a trade secret. As far as possible, a knowledge of the composition of the natural oil serves as a guide in choosing the constituents; in the blending of perfumes the best results appear to be obtained by the addition of both natural and synthetic products. Thus, in the group of perfumes, jasmine, lilac, muguet, &c., jasmine oil is added to a mixture of synthetic substances.

Bergamot. The natural oil contains about 38 p.c. of linalyl acetate: other constituents are limonene, di-pentene, linalool, camphene, octylene, acetic acid (Burgess and Page, Chem. Soc. Trans. 1904, 85, 1327), and two substances of unknown constitution, bergaptene

$$C_{11}H_5O_3{\cdot}OCH_3$$

(Pomeranz) and bergaptine, a coumarin-like substance, melting at 59·5° (Soden and Rojahn, Pharm. Zeit. 46, 778). The main constituent of the synthetic oil is linalyl acetate; terpineol acetate, geranyl propionate, and geranyl methyl ether are also used in its preparation.

Carnation. Eugenol, *iso*eugenol, caryophyllene are used as ingredients of oil of carnation.

Hawthorn. The scent of the hawthorn is faithfully reproduced by anisaldehyde (Aubépine).

Heliotrope. Attempts to identify heliotropin in the extract of heliotrope flowers have failed; the odour of synthetic heliotropin closely resembles that of the heliotrope flower and is the basis of all the heliotrope perfumes. Its odour is improved by the addition of coumarin and vanillin and by blending with rose or jasmine oil.

Hyacinth. Enklaar (Chem. Weekblad, 1, 1910, 7) identified benzyl alcohol, benzyl benzoate, and ethyl cinnamate in the essential oil of hyacinth; he failed to detect methyl anthranilate. Cinnamic alcohol is especially characterised by a hyacinth-like smell. The following constituents are used in preparing an oil of hyacinth: phenyl ethyl alcohol, cinnamic alcohol, phenyl ethyl aldehyde, methyl benzoate, phenyl ethyl acetate, methyl and ethyl cinnamates, terpineol, and α-chlor- and α-bromstyrolenes.

Jasmine. The oil extracted from the pomade obtained from jasmine flowers by the process of enfleurage was shown by Hesse to have the following composition (Ber. 1899, 32 2611):

Benzyl acetate . .	65·0 p.c.
Linalyl acetate . .	7·5 ,,
Benzyl alcohol . .	6·0 ,,
Linalool	16·0 ,,
Indole	2·5 ,,
Methyl anthranilate . .	0·5 ,,
Jasmone (a ketone $C_{11}H_{16}O$)	3·0 ,,

The methyl anthranilate cannot be extracted directly from the plant, but appears to be formed during the process of enfleurage. By distillation with steam, 0·4 p.c. methyl anthranilate was obtained. The oil obtained by distilling the fresh flowers was found to be free from indole (Hesse, Ber. 1904, 37, 1457).

Elze (Chem. Zeit. 1910, 34, 912) found, in addition to the above, cinnamyl acetate, geraniol, *p*-cresol, and *p*-cresyl methyl ether. The synthetic oil consists chiefly of benzyl acetate and benzyl alcohol to which cinnamic acetate, linalool and its acetate, indole and methyl anthranilate may be added. The substance peculiarly characteristic of the jasmine scent appears to be the ketone jasmone, which cannot yet be obtained synthetically. A proportion of jasmine oil is generally added to the mixture of synthetic substances, as the oil prepared only from synthetic substances is not entirely satisfactory.

Lilac. Terpineol is the characteristic constituent of lilac perfumes. Commercial terpineol is prepared by the action of dilute acids on terpin hydrate, the fraction boiling up to 216°, being known as terpinol and terpinolene, above 216° as terpineol. Commercial terpineol is obtainable both in the solid and liquid forms, the latter having the more intense odour. It contains both di-pentene and terpinolene.

Lily of the Valley (Muguet). Terpineol is also used as a constituent of the lily of the

valley perfumes with geraniol and citronellol. A mixture of 90 p.c. terpineol and 10 p.c. palma rosa oil has a strong muguet odour. Linalool, benzyl alcohol and its acetate are amongst the other constituents employed.

Musk. Natural musk, obtained from an abdominal gland of the musk deer (*Moschus moschiferus*), owes its characteristic odour to a ketone, muscone ($C_{15}H_{30}O$ or $C_{15}H_{28}O$); the distillate obtained on distilling the secretion in steam is extracted with ether, treated with alcoholic potash, washed with water and finally distilled *in vacuô*. The ketone passes over in the fraction boiling at 145°–147° (3 mm.). Muscone is now sold in alcoholic solution. The isolation from civet of a ketone $C_{17}H_{30}O$, designated civetone, has also been described; it melts at 32·5°, boils at 204°–205° (17 mm.), and yields a semi-carbazone, melting at 189° (Sack, D. R. P. 279313). As early as 1759, Margraff had obtained a product smelling of musk by treating amber with nitric acid. In 1878, von Gerichten observed the musk-like odour of chlor- and brom-nitrocymenes and three years later, Kolbe prepared another musk-scented compound, di-nitro-*m*-cymene. In 1888, Baur took out the first patents for the preparation of artificial musk and has since made an exhaustive study of the groups in the benzene ring conditioning the musk-like odour. The nitro- groups must be present, and a third negative group symmetrically arranged; the three other positions are filled by alkyl groups, of which one must be a tertiary radicle. A large number of these artificial musks, di-nitro- or tri-nitro- derivatives of tert-butyl-toluene or -xylene, have been introduced. The most important of these are:

Musc Baur Moschus . Tonquinol .	Trinitro-tert-butyltoluene
	Trinitro tertiary-butylxylene
Musk ketone	Dinitro-tert-butyl-*m*-xylyl methyl ketone
Musk aldehyde	Dinitro-butyl-*m*-xylyl aldehyde.

Orange-flower (synthetic neroli oil). The composition of a specimen of the natural oil is given as follows (Hesse and Zeitschel, J. pr. Chem. 1902, [ii.] 66, 481):—

	p.c.
Hydrocarbons (pinene, camphene, dipentene and a paraffin C_{27}) . .	35·0
Terpene alcohols and acetates—	
l-Linalool	30·0
l-Linalyl acetate	7·0
d-Terpineol	2·0
Geraniol and nerol . . .	4·0
Geranyl and neryl acetates . .	4·0
d-Nerolidol	6·0
Methyl anthranilate	0·6
Acetic and palmitic acids . . .	0·1
Indole	0·1
Resin and loss (decylic, phenyl acetic acids, &c.)	11·2
	100·0

Farnesol has subsequently been identified.

Methyl and ethyl β-naphthyl ethers are employed as substitutes for neroli oil; a mixture of the two was originally introduced as nerolin, the former is now known as yara-yara, the latter as bromelia. In the composition of the synthetic oil, geraniol, linalool, nerol, and their acetates with methyl anthranilate are used. A solution of 40 grams of the synthetic oil in 1 kg. of alcohol constitutes the tincture used as the equivalent of the first infusion of the flower pomade.

Rose. The natural oil was shown by Markownikoff in 1891 (Ber. 23, 3191) to consist of an inodorous hydrocarbon, stearoptene, melting at 36·5° and a liquid portion, eleoptene, from which two substances, having the composition $C_{10}H_{18}O$ and $C_{10}H_{20}O$, could be separated. In the same year, Poleck and Eckart (*ibid.* 23, 3554) showed that the liquid constituent $C_{10}H_{18}O$ (rhodinol) was identical with geraniol, isolated by Semmler from Indian geranium oil and constituting 66–74 p.c. of German and 80–88 p.c. of Turkish rose oil. The presence of citronellol ($C_{10}H_{20}O$) was established by Tiemann (Ber. 29, 921), who, by treating the alcohols at a low temperature with PCl_3 in ethereal solution, obtained a phosphite of citronellol, geranyl chloride remaining in the ethereal solution. These two alcohols form the main constituents of rose oil and of such preparations as roseol, reuniol, &c. In 1900, it was shown that the extract of fresh rose-leaves contained about 2 p.c. of phenyl ethyl alcohol. This was present to a much less extent in the oils obtained by steam distillation, owing probably to the loss of the sparingly soluble alcohol in the steam distillate. In addition to the above alcohols, small amounts of farnesol, linalool, citral, and nonaldehyde were detected (Walbaum, Ber. 1900, 33, 2299, 2302; *cp.* Soden and Rojahn, *ibid.* 1900, 33, 3063; Schimmel, Rep. 1900, 53). The substances enumerated above are used in the manufacture of synthetic rose oil, and traces of the higher fatty aldehydes containing from 8 to 12 carbon atoms have been added. Up to the present, the scent of the oil prepared entirely from synthetic substances cannot rival the fragrance of the natural product. The most successful preparations contain some proportion of the natural oil or of the tincture made from the natural extract, to which some synthetic rose oil and such substances as neroli oil, vanillin, musk, or other synthetic compounds may be added at the discretion of the perfumer. Extensive adulteration of the natural oil takes place at the source of production, *e.g.* in Bulgaria, the geraniol and citronellol from cheaper oils, such as geranium, palma rosa, being added and distilled with the rose oil.

Violet. The basis of the artificial violet perfumes is ionone or some closely allied substance. The scent of α-ionone is stated to be sweeter and more penetrating, resembling more closely that of orris root; that of the β- compound resembles more closely the natural violet. After smelling a natural violet extract or a solution of ionone for some little time, the odour often cannot be perceived, the nasal nerve-endings being easily fatigued by this scent. The smell of violets is only apparent when the pure substance is diluted. Ionone was originally placed on the market as a 10 p.c. alcoholic solution, 10 grams of which gave 1 kilogram of violet tincture. Now the pure substances, consisting of 100 p.c. α-ionone and 100 p.c. β-ionone

respectively are obtainable. Irone and derivatives of ionone also find application. With the violet tincture so prepared, other tinctures made both from natural and synthetic oils are blended: rose, jasmine, orris, ylang-ylang, are amongst those thus used. As instances of violet scents prepared from natural and synthetic substances, the following may be quoted (Mann, Moderne Parfumerie):—

Spring violet.		Violet scent.		
grms.		grms.		
6000	Infusion violets, I.	5000	Tincture ionone	Synthetic
2000	,, rose, I.	1000	,, rose-oil	Synthetic
750	,, jasmine, I.	1000	,, jasmine	Synthetic
250	,, acacia	300	,, orange	Synthetic
50	Tincture coumarin	3000	,, iris oil	Synthetic
50	Infusion benzoin	50	,, musk	Synthetic
50	,, musk	10	Ylang-ylang oil	Synthetic
100	Solution rose oil	200	Infusion benzoin	
100	Tincture vanillin			
40	,, viodoron			

Ylang-ylang oil. The oil extracted from the flowers of *Cananga odorata* (Hook) (*v.* OILS, ESSENTIAL) contains about 30–32 p.c. linalool, 9 p.c. linalyl benzoate, 7 p.c. linalyl acetate, a little geraniol, and about 30 p.c. of a hydrocarbon, cadinene. Methyl alcohol and *p*-cresyl acetate have also been detected (Darzens, Bull. Soc. chim. 1902, 27, 83). Bacon identified in addition formic acid and *iso*safrol (Schimmel, Rep. Oct. 1908). In the composition of the artificial oil, the following compounds occur: ilnalool, geraniol, methyl and ethyl benzoates, linalyl and geranyl benzoates, benzyl salicylates and other esters. Bacon (*l.c.*) also examined a number of esters with reference to their suitability as constituents of this oil.

New mown hay. Coumarin forms the main constituent of this perfume and with it tinctures of orange, rose, jasmine, &c., are blended.

As instances of two well-known fancy perfumes, the following may be quoted (Mann, Moderne Parfumerie). These are, of course, subject to wide variation.

Peau d'Espagne.		Ess bouquet.	
grms.		grms.	
50	Cassie flower oil	2000	Tincture of rose, I.
100	Sandalwood oil	1000	,, cassie, I.
60	Niobe oil	1000	,, tuberose, I.
200	Bergamot oil	2550	Extract of reseda
1000	Tincture of musk	2000	,, bergamot
1500	,, civet	10	Rosewood oil
1000	Infusion of tolu	50	Bergamot oil
40	Vetiver oil	100	Infusion of musk, I.
10	Turan oil	50	Tincture of civet
10,000	Spirit	100	Infusion of tolu
		3	Turan oil

Eau de Cologne. This, one of the oldest and most famous of perfumes, was manufactured in Cologne at the end of the seventeenth century. It is disputed whether Johann Maria Farina or Paul de Feminis of Milan, both of whom came from Italy to Cologne, was the original inventor; in both cases the secret was bequeathed to their successors, that of Paul de Feminis passing to his nephew, Johann Anton Farina: there are now three firms bearing the name Farina who claim to possess the original formula and who zealously guard it. The general nature of the preparation of Eau de Cologne is, however, known, although details of the preparation may be lacking. The quality of the spirit used is of paramount importance: only the most highly purified spirits of wine may be used, and after the perfume is prepared, it must be left for a long time, some years if possible, to mature. The firms who possess the original secret continue to use the same ingredients and are not concerned with synthetic oils. Other perfumers make use of such synthetic oils as nerol and bergamot, with those of rosemary, lemon, lavender, and petit-grain; the composition of each Eau de Cologne varies considerably. A typical example is as follows:—

30,000	grams	spirit.
100	,,	neroli oil.
30	,,	rosemary oil.
100	,,	Mitcham lavender oil.
300	,,	lemon oil.
300	,,	bergamot oil.
50	,,	petit-grain oil.

(*See* OILS, ESSENTIAL; Gildemeister und Hoffmann, Die Aetherischen Oele, 1910, Otto, Les Parfums; Chemistry of Essential Oils and Artificial Perfumes, Parry, 1919; &c.). I. S. M.

PERHYDROL. Trade name for a solution of hydrogen peroxide (*q.v.*).

PERI ACID. S. acid. 1-Naphthylamine-8-sulphonic acid *v.* NAPHTHALENE.

PERICLASE. Magnesia crystallised in the cubic system. The natural mineral varies somewhat in composition, and consequently also in density, owing to isomorphous replacements, as shown in the following analyses: I, from Vesuvius (A. Damour, 1843); II, from Nordmark, Sweden (A. Sjögren, 1887); III, artificial crystals (A. B. de Schulten, 1898):

	I.	II.	III.
MgO	93·86	86·38	99·92
FeO	5·97	0·46	trace
MnO	—	8·27	—
ZnO	—	1·98	—
H_2O	—	1·45	—
	99·83	98·54	99·92
Sp.gr.	3·67	3·90	3·566

The mineral occurs as small, colourless to green octahedra, cubes, or grains with a perfect cubic cleavage. Hardness about 6. Refractive indices (Na) at 24° 1·7378, at 650° 1·7488 (for artificial crystals containing MgO 99·25 p.c., Fe trace, O. Westphal, 1913).

When moistened with water, the mineral shows an alkaline reaction, and it is readily soluble in acids. Small crystals and grains, usually surrounded by a zone of brucite, are rarely found scattered through crystalline limestones, *e.g.* in the blocks enclosed in Vesuvian lava; with manganese ores at Nordmark and Långban in Sweden; at Predazzo in Tyrol; and Riverside in California. A dolomite or a magnesian limestone when baked by contact with an igneous rock-mass (contact metamorphism) becomes dedolomitised; the calcium carbonate crystallising as granular calcite, and the magnesia separating as periclase in the absence of silica and alumina. Usually, however, the rock contains sufficient silica and alumina as impurities for the formation of various magnesium silicates (forsterite, diopside, tremolite, chondrodite) and spinel, which are of common occurrence in metamorphosed limestones. If periclase is present in the purer marbles, it is usually altered by hydration into brucite ($Mg(OH)_2$), and by further alteration

into hydromagnesite ($3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$). The so-called predazzite and pencatite from the Tyrol consist of such intimate intermixtures of calcite and brucite that they were formerly regarded as mineral species with the formulæ

$$2CaCO_3 \cdot Mg(OH)_2 \text{ and } CaCO_3 \cdot Mg(OH)_2$$

respectively.

Well-developed octahedral crystals of periclase measuring up to 1 cm. along the octahedral edge, have been obtained artificially by the action of lime on magnesium borate or magnesium chloride at high temperature; by the action of hydrochloric acid gas on magnesia; by heating magnesia in fluxes of magnesium chloride, silica, or potassium hydroxide; and from the pure melt in the electric arc. Minutely crystallised periclase is also the main constituent of refractory magnesia bricks. F. Cornu (1908) found a Styrian brick to consist of 94 p.c. of periclase set in a vitreous cement. Enclosed in the grains of periclase were skeletal growths of magnesioferrite ($MgFe_2O_4$, a member of the spinel group). L. J. S.

PERICLINE *v.* FELSPAR.

PERIDOT *v.* OLIVINE.

PERIDOTITE. A plutonic igneous rock composed mainly of olivine (peridot). Other ferro-magnesian minerals (augite, enstatite, hornblende, biotite), together with magnetite, ilmenite, chromite, picotite, garnet, etc., but not felspar, may be present, and several varieties are accordingly distinguished. Peridotite is therefore rather the name of a group of ultrabasic rocks, which contain: SiO_2 35–45, Al_2O_3 0–6, FeO 8–10, CaO 0–2, MgO 35–48 p.c., with only traces of alkalis; sp.gr. 3·0–3·3. The more important varieties are: *Dunite*, from Dun Mountain in New Zealand, consists of olivine with some chromite; *Lherzolite*, from Lake Lherz in the Pyrenees, of olivine, diallage, and hypersthene; *Harzburgite* and *Saxonite*, from Harzburg in the Harz and from Saxony, of olivine and enstatite. These rocks form large bosses or dykes, and have often arisen by the modification by magmatic segregation of gabbro magmas. They are of importance as mother-rocks of certain ores and minerals, *e.g.* platinum, iridosmine, awaruite (a native nickel-iron), diamond, pyrope-garnet, some rubies, nickel and chromium ores, &c. By their alteration they have given rise to large masses of serpentine-rock with associated secondary magnesium minerals such as magnesite, meerschaum, &c. Meteoric stones, which consist mainly of olivine and enstatite, have very much the same chemical and mineral composition as certain peridotites. L. J. S.

PERILLALDEHYDE $C_9H_{13} \cdot CHO$, a lævorotatory liquid, b.p. 104°/9 mm., of unknown constitution, forming 44–57 p.c. of the esssential oil of the leaves of *Perilla nankinensis* (Dene), a labiate known in Japan as 'Shiso.' The leaves are used as a condiment or vegetable. According to Furukawa and Tomizawa the α-anti-aldoxime of perillaldehyde is the sweetest substance known, being two thousand times sweeter than sucrose and four to eight times as sweet as saccharin. Its isomeride *β-syn* aldoxime is not at all sweet (Furukawa, Jap. Pat. 35332).

PERILLA OIL. Perilla oil occurs to the extent of about 35·8 p.c. in the nuts of *Perilla ocymoides* (Linn.), an annual labiate, indigenous to the East Indies as also to China (Manchuria) and Japan. It is extensively grown in China and Japan, and is also cultivated in the Himalayas. The plant is sown in April, blossoms about the end of September, and ripens two weeks later. The seed is known in Japan as Ye-Goma, or Se-no-abura. The oil has the following characters: sp.gr. 0·928 at 20°; $n_D^{20} = 1{\cdot}4830$; sapon. value 187·4; iodine value (Hanus) 204·3; hexabromide value 50·8. The mixed fatty acids separated by the lead salt-ether method give 12 p.c. of saturated acids and 88 p.c. of unsaturated acids. The saturated portion consists mainly of palmitic acid. The unsaturated acids when oxidised give a hexahydroxystearic acid of m.p. 165°. A tetrahydroxystearic acid of m.p. 135°–140° is also formed. The fatty acids of perilla oil appear therefore to consist of palmitic, a linolic, and several geometrically isomeric linolenic acids (Bauer, Farben. Zeit. 1922, 27, 2756; Chem. Umschau, 1923, 30, 9). See also tables under OILS, FIXED, AND FATS.

This oil has the highest iodine value of any known fatty oil, and resembles linseed oil in taste and smell. Endeavours have been made to import it into Europe as a substitute for linseed oil.

For the essential oil of *Perilla citriodora*, which mainly consists of citral, *v.* Kondo and Yamaguchi (J. Pharm. Soc. Japan, 1919, 446, 263).

PERISTALTIN. A patent preparation used as a purgative, obtained from the bark of *Rhamus purshiana* (Cascara sagrada). Yellow bulky powder, soluble in water or alcohol, sparingly soluble in acetone, insoluble in ether or light petroleum. Contains a reducing sugar, giving a phenylosazone, m.p. 208°. Appears to be a mixture of glucosides, and on hydrolysis by steam yields rhamnose, chrysophanic acid (chrysophanol), emodin methyl ether, and *cascarol* $C_{15}H_{10}O_5$ m.p., 218°, forming yellow needles, from pyridine, alcohol, or acetone. Insoluble in water, chloroform, ether, or cold sodium hydroxide solution; yields a crystalline *acetyl* derivative, m.p. 204°–205° Tschirch and Monikowski, Arch. Pharm. 1912, 250, 92).

PERISTERITE *v.* FELSPAR.

PERMANGANATES *v.* MANGANESE.

PERMIDAN. Trade name for dimethylaminopyrazolone.

PERMONITE. An explosive consisting of a mixture of ammonium nitrate, potassium chlorate, trinitrotoluene, starch, and wood meal.

PERNAMBUCO WOOD *v.* BRAZIL WOOD.

PEROCIDE. Trade name for a mixture of the sulphates of the cerite earths, obtained as a by-product in the manufacture of incandescent mantles; used as a fungicide. Uusally contains 43–47 p.c. of cerite earth oxides (Mach and Lederle, Chem Zeit. 1919, 43, 117).

PEROFSKITE or **PEROVSKITE** *v.* TITANIUM.

PERONIN. Trade name for the hydrochloride of morphine benzyl ester, used as a sedative (*v.* SYNTHETIC DRUGS).

PERONINE *v.* OPIUM.

PEROXOLS. Trade names for mixtures of hydrogen peroxide containing salicylic acid,

carbolic acid, β-naphthol, thymol, camphor, menthol, &c. Used as disinfectants.

PEROXYDASES *v.* FERMENTATION.

PERSEITOL *v.* CARBOHYDRATES.

PERSIAN BERRIES are the seed-bearing fruit of various species of *Rhamnus*, growing wild or cultivated in France, Spain, Italy, the Levant, and Persia. The Persian berry proper is obtained from *R. amygdalinus*, *R. oleoidis*, and *R. saxatilis*, and is imported from Smyrna and Aleppo. Its size is about that of a pea, colour yellowish-green, surface much shrivelled, hard, and divisible along well-marked depressions forming a cross, into four parts, each containing a triangular seed; its taste is intensely bitter.

Avignon or French berries, the product of *R. infectorius* (Linn.) and *R. alaternus* (Linn.), are smaller in size than the foregoing and contain only two seeds.

Spanish, Italian, and Hungarian berries are respectively the products of *R. saxatilis*, *R. infectorius* (Linn.), and *R. cathartica* (Linn.). These are similar in quality to the Avignon berries. Other qualities come from the Morea, Wallachia, and Bessarabia.

All of these botanical varieties do not contain entirely the same constituents, but, on the other hand, there is every reason to suppose that the colouring constituents of those to which the term Persian berry proper is applied are identical in each case.

Gelatly (Edinburgh New Phil. Jour. 7, 252) was the first to isolate from Persian berries (*R. tinctoria*, Wald. et Kit.) the glucoside *xanthorhamnin* $C_{45}H_{56}O_{28}$, which on hydrolysis with acid gave a sugar and a colouring matter *rhamnetin*. Hlasiwetz (Annalen, 112, 107) considered that xanthorhamnin was identical with quercitrin, and rhamnetin with quercetin, but Schützenberger and Bertèche (Bull. Soc. Ind. Mulhouse, 35, 456) denied this, and assigned to rhamnetin the formula $C_{12}H_{10}O_5$. Xanthorhamnin, which Schützenberger (Jahres. 1868, 774) termed *α-rhamnegin*, was considered to possess the formula $C_{24}H_{32}O_{14}$. The presence of a second glucoside, *β-rhamnegin*, was also detected by this chemist, and from this by hydrolysis *β-rhamnetin* was derived. Liebermann and Hörmann (Annalen, 196, 313) also investigated Persian berries, devised a method for the preparation of xanthorhamnin and rhamnetin, and prepared various derivatives of the latter.

It is now known that Persian berries contain the glucosides of three colouring matters, namely rhamnetin, rhamnazin, and quercetin (Herzig, Monatsh. 6, 889; 9, 549; 12, 175; Perkin and Geldard, Chem. Soc. Trans. 1895, 67, 500).

To isolate these substances Persian berries are extracted with boiling water, the solution treated with a small quantity of sulphuric acid, and digested while boiling for one hour. The glucosides are thus hydrolysed and the crude colouring matters separate in the form of a greenish-yellow precipitate.

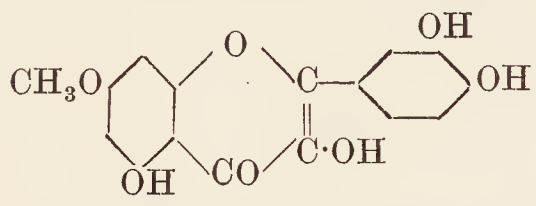
The product is extracted with boiling alcohol, which dissolves principally the *quercetin*, this being the most soluble of the three colouring matters. The residue now contains rhamnetin and rhamnazin, and the latter is removed from the former by two or three extractions with boiling acetic acid.

Rhamnetin $C_{16}H_{12}O_7$ crystallises in yellow needles very sparingly soluble in acetic acid and alcohol. It dissolves in alkaline solutions with a pale yellow colour, and gives with alcoholic lead acetate an orange-red precipitate. When acetylated it forms *tetra-acetylrhamnetin* $C_{16}H_8O_7(C_2H_2O)_4$ (Liebermann and Hörmann), colourless needles, m.p. 183°–185°, and on bromination *dibromrhamnetin* is produced.

Rhamnetin sulphate $C_{16}H_{12}O_7 \cdot H_2SO_4$ (Perkin and Pate, Chem. Soc. Trans. 1895, 67, 650), orange-red needles, and *monopotassium rhamnetin* $C_{16}H_{11}O_7K$ (Perkin and Wilson, *ibid.* 1903, 83, 136), orange-yellow needles, have been prepared.

Rhamnetin is in reality a *quercetinmonomethyl ether* (Herzig, *l.c.*), for on digestion with hydriodic acid it is converted into *quercetin*, and when methylated with methyl iodide *quercetintetramethyl ether* is produced.

By the action of boiling potassium hydroxide solution, of boiling alcoholic potash, or by aspirating air through its alkaline solution, rhamnetin gives *protocatechuic acid*, and a syrupy phloroglucinol derivative. The latter, identified by means of its diazobenzene compound, consists of *phloroglucinol monomethyl ether* (Perkin and Allison, Chem. Soc. Trans. 1902, 81, 470), and consequently the constitution of rhamnetin is to be expressed as follows:—



Rhamentin is a strong dyestuff, and gives on mordanted woollen cloth shades which are practically identical with those produced by quercetin:—

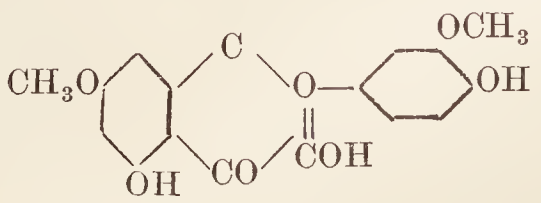
Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Red-brown.	Brown-orange.	Bright orange.	Deep olive.

(Perkin and Wilkinson, *ibid.* 1902, 81, 590).

Rhamnazin $C_{17}H_{14}O_7$ (P. and G.), yellow needles, m.p. 214°–215°, is moderately soluble in boiling toluene, a property which distinguishes it from both rhamnetin and quercetin. It dissolves in alkaline liquids to form orange-yellow solutions, and with alcoholic ferric chloride gives an olive-green coloration.

Acetylrhamnazin $C_{17}H_{11}O_7(C_2H_3O)_3$, colourless needles, *benzoylrhamnazin* $C_{17}H_{11}O_7(C_7H_5O)_3$, colourless needles, m.p. 204°–205°, and *dibromrhamnazin* $C_{17}H_{12}Br_2O_7$, yellow needles, have been prepared.

Rhamnazin is a *quercetin dimethyl ether*. Digested with boiling hydriodic acid, it is converted into quercetin, and by methylation in the ordinary manner gives quercetin tetramethyl ether. Boiling alcoholic potash hydrolyses rhamnazin with formation of *vanillic acid* and *phloroglucinol monomethyl ether* (Perkin and Allison, *l.c.*). It accordingly possesses the constitution—



Rhamnazin does not readily dye mordanted calico, but on mordanted wool gives shades resembling those which are produced by kaempferol—

Chromium.	*Aluminium.*	*Tin.*	*Iron.*
Golden-yellow.	Orange-yellow.	Lemon-yellow.	Olive-brown.

Only a small amount of this colouring matter is present in Persian berries.

Xanthorhamnin $C_{34}H_{42}O_{20}$ is readily prepared by extracting powdered Persian berries with three times their weight of boiling 85 p.c. alcohol. On standing the dark brown filtered extract deposits a large quantity of the impure glucoside as a brown resinous mass. From the supernatant liquid on standing a purer xanthorhamnin separates in the form of a pale yellow cauliflower-like precipitate, and in such quantity as to congeal the whole liquid to a stiff paste. This is collected, repeatedly crystallised from alcohol, and finally from alcohol containing a little water and ether (Liebermann and Hörmann, *l.c.*).

Xanthorhamnin consists of pale yellow needles readily soluble in water and hot alcohol, soluble in alkaline solutions with a yellow colour. With basic lead acetate it gives an orange precipitate. According to the work of Liebermann and Hörmann, xanthorhamnin, when hydrolysed with acid, gives *rhamnetin* and *rhamnose*

$$C_{48}H_{66}O_{29}+5H_2O=4C_6H_{14}O_6+2C_{12}H_{10}O_5$$

More recently, however, xanthorhamnin has been shown to possess the formula $C_{34}H_{42}O_{20}$, and that by means of its specific ferment *rhamninase*, contained by Persian berries, it is hydrolysed with formation of rhamnetin and a complex sugar *rhamninose* $C_{18}H_{32}O_{14}$

$$C_{34}H_{42}O_{20}+H_2O=C_{16}H_{12}O_7+C_{18}H_{32}O_{14}$$

When rhamninose is digested with boiling dilute acids, it is converted into 2 molecules of *rhamnose* and 1 molecule of *galactose* (C. and G. Tanret, Compt. rend. 1899, 129, 725)

$$C_{18}H_{32}O_{14}+4H_2O=C_6H_{12}O_6+2C_6H_{14}O_6$$

No glucosides of rhamnazin or quercetin have been isolated as yet from Persian berries.

The action of the ferment rhamninase is readily demonstrated. If crushed Persian berries, contained in a muslin bag, are suspended in water heated to 40°, a yellow solution containing the glucosides is produced; this quickly becomes opaque and a heavy precipitate of the mixed colouring matters eventually separates. To within recent years this reaction was carried out on a commercial scale, and the product was placed on the market under the name of 'rhamnétine.' This reaction can be employed to distinguish between the dyeing properties of the glucosides contained in the berries, and the free colouring matters produced by their hydrolysis. Thus if Persian berries be added to a cold dye-bath, and this is slowly heated to boiling, the glucosides are hydrolysed by the ferment; but if, on the other hand, the berries be at once plunged into boiling water, the ferment is killed and a solution of the glucosides is obtained. In the former case wool mordanted with tin gives an orange-red shade, whereas in the latter a pure yellow colour is produced.

Beyond the ordinary extract of Persian berries which is prepared in large quantity by extracting the berries with boiling water, and evaporating the solution under reduced pressure, no special commercial preparations are manufactured at the present time.

Dyeing properties.—In wool dyeing Persian berries are little employed on account of their cost; moreover, they possess no special advantage over quercitron bark and old fustic. Persian berries, as a rule, give redder shades than quercitron bark, a fact which is to be explained as due to the hydrolysis of its glucosides by the ferment. The quercitrin of quercitron bark is not accompanied by such a specific ferment, and consequently the shades given by this dyestuff are of a yellower character. With tin mordant Persian berries give bright yellows and oranges, which are only fairly fast to light; but according to Hummel, the yellowish-olive produced with copper mordant is extremely fast, and is darkened rather than otherwise by exposure. Persian berries are still used to a considerable extent in calico-printing for the formation of yellow, orange, and green shades. A. G. P.

PERSIAN GREEN. *Emerald green v.* PIGMENTS.

PERSIAN RED. *Basic lead chromate v.* CHROMIUM.

PERSIMMON, the fruit of *Diospyros virginiana* (Linn.), much cultivated in Japan, and now in California and other warm countries. When freshly gathered, the fruit has a very astringent taste, which it loses on keeping, especially if exposed to a low temperature.

König gives as its average composition—

Water	Protein	Invert sugar	Cane sugar	Other N-free extract	Fibre	Ash
66·1	0·8	13·5	1·0	16·0	1·8	0·9

Tannin is abundant in the freshly gathered fruit, but on storage is deposited in an insoluble form, in certain specialised cells (Bigelow, Gore and Howard, J. Amer. Chem. Soc. 1906, 28, 688). H. I.

PERSULPHURIC ACID and **PERSULPHATES** *v.* SULPHUR.

PERTHITE *v.* FELSPAR.

PERU BALSAM *v.* BALSAMS.

PERYLENE (*peri*-dinaphthylene). A hydrocarbon $C_{20}H_{12}$ obtained by heating either naphthalene, or 1 : 1′-dinaphthyl with aluminium chloride; or by heating 1 : 8-di-iodonaphthalene with finely divided copper. The best result is obtained by the condensation of 4 : 4′-dicyano-1 : 1′-dinaphthyl to 3 : 10-dicyanoperylene $C_{22}H_{10}N_2$, brown microscopic needles, m.p. 368°–369°, soluble in acetic acid or xylene with intense green fluorescence. It may also be obtained by heating 2 : 2′-dihydroxyl-1 : 1′-dinaphthyl to 400°–500° with PCl_5 or PCl_3 (Hansgirg and Zinke, Monatsh. 1919, 40, 403). Glistening yellow crystalline leaflets, m.p. 264°–265°, forming yellow to reddish-yellow solutions with a blue fluorescence (Scholl, Seer and Weitzenböck, Ber. 1910, 43, 2202; Weitzenböck, Seer and Bartsch, Ber. 1913, 46, 1994). *Perylene-hexahydride* $C_{20}H_{18}$, prepared by heating perylene with hydriodic acid and red phosphorus at 200°–210°; rhombohedral crystals, m.p. 182°–183°. *Trinitro-* and *tetranitroperylene* are

formed by heating perylene with nitric acid (Zinke and Unterkreuter, Monatsh. 1919, 40, 405).

PETALITE. A lithium aluminium silicate $LiAl(Si_2O_5)_2$ containing 4·9 p.c. lithia, and much resembling spodumene $[LiAl(SiO_3)_2]$ in appearance. The lithium is usually partly replaced by sodium, and to a less extent by potassium; analyses showing Li_2O 2·62–4·22 p.c. Crystals are monoclinic, but of rare occurrence; the mineral usually forming platy, cleavable masses (hence the name, from πέταλον, a leaf) of a white, grey, or pinkish colour and with a vitreous lustre; sp.gr. 2·4 (that of spodumene being 3·16); H. 6–6½. It is found, together with other lithium-bearing minerals (lepidolite, tourmaline, and spodumene), in an iron mine on the island of Utö near Stockholm, where it has been mined as a source of lithium salts. It was in this mineral that lithium was discovered by J. A. Arfvedson in 1817. Other localities are Peru in Maine, and Bolton in Massachusetts. A colourless, glassy variety, known as castorite, is found in the granite of the island of Elba. L. J. S.

PETIT-GRAIN OIL *v.* OILS, ESSENTIAL.

PETROFRACTEUR. An explosive resembling *kinetite* (*v.* EXPLOSIVES) in composition, but differing specially in that it contains no gun-cotton. Is said to consist of a mixture of 10 p.c. nitrobenzene, 67 p.c. potassium chlorate, 20 p.c. potassium nitrate, and 3 p.c. antimony pentasulphide (*v.* Watson Smith, J. Soc. Chem. Ind. 1887, 5).

PETROLEUM.

AMERICAN PETROLEUM.

1. *Occurrence.*

Three closely-related mineral substances, all belonging to the class of bitumens, occur usually associated together. These are natural gas, liquid petroleum, and solid natural paraffin or ozokerite. Occasionally petroleum is found alone; usually natural gas and petroleum are found together. Less frequently, natural paraffin wax is found with the other two bitumens filling interstices in oil rocks. Paraffin is generally found dissolved in petroleum. Generally a fourth bitumen, asphaltum, is found suspended in petroleum or as semi-solid 'tar' or 'pitch.' Lately paraffin has been found and obtained industrially from petroleum which contains much asphalt, but, as a rule, petroleums are roughly divided into 'paraffin base' and 'asphaltic base,' according to the predominance of one or the other, and sufficient paraffin wax for commercial needs is obtained from the paraffin base oils. It is unnecessary to separate wax from the more complex asphaltic oils.

America produced over two-thirds of the world's petroleum in 1920. The United States produced 443,402,000 barrels (61,669,263 metric tons), or 66 p.c. of the world's total of 687,190,251 barrels (95,575,834 metric tons). About three-fifths of the American product is paraffin base oil. The oil-fields of North America occur in widely separate areas, and are grouped usually as the (*a*) Appalachian, (*b*) Lima (Ohio)-Indiana, (*c*) Illinois, (*d*) Mid-Continent, (*e*) Gulf Coast, (*f*) Rocky Mountain, (*g*) Pacific Coast, (*h*) Canadian, and (*i*) Mexican, fields.

The Appalachian field includes many small oil pools scattered over western New York, western Pennsylvania, West Virginia, eastern Ohio, Kentucky, and Tennessee. The American oil industry began in 1859, with the drilling of the Drake well, near Titusville, in western Pennsylvania. Oil was obtained at 57 feet. The exigencies of caring for the product of many shallow wells quickly drilled in that region necessitated the rapid development of tank cars and pipe-lines. In fact, this region originated many of the modern engineering features of oil-well production, distribution, and utilisation. The oil pools spread to the north into New York, and south into West Virginia, and, to a minor degree, into Kentucky and Tennessee, and into eastern Ohio. For many years the adequacy of this field stopped inquiry as to oil possibilities in other States.

Kentucky's eastern oil-fields date back to the beginning of the oil industry. They yield paraffin oils of fair quality, but production is small. New extensions in Estill and neighbouring counties have lately increased the production significantly. In western Kentucky many very shallow wells (300 to 1000 feet) are producing oil with more than the average amount of sulphur. The oil is found just under the Chattanooga black shale, and as this formation underlies a very great territory, much significance attaches to the development. Similar conditions are found in Tennessee.

The oils of the Appalachian system are found in sand-stone lenses contained in shales. The wells are generally from 1800 to 3000 feet deep. Many other wells have been successful at greater depths. Large quantities of natural gas have lately been obtained in Westmoreland County, Pennsylvania, in a well 6822 feet deep. Usually the oil and gas have accumulated in anticlinal structures. In the Appalachian field several 'oil sands' may be found in one well, such as the 'first,' 'second,' and 'third,' and 'Venango' sands.

Lima (Ohio)-Indiana Field.—Meanwhile, natural gas was found in sufficient quantities for domestic heat and light in a small hamlet called East Rockport, Ohio, on the south shore of Lake Erie. This eventually led to the development of monster gas wells in central Ohio. Some of them yielded petroleum so contaminated with organic sulphur compounds as to limit its use to fuel purposes. A successful process of eliminating the sulphur was finally developed, and this oil (Lima oil) has since yielded gasoline, lamp oils, lubricants, etc., as satisfactory as those from Appalachian petroleum. The oil-pools spread into Indiana, but the pools have declined to small proportions. The oil is found in limestones of Ordovician age. The rock has been altered to dolomite, leaving vacant spaces within the crystalline mass sufficient for oil storage. The anticlinal structures which have served to accumulate the oil are incidents in the great geoanticline called the Cincinnati Arch.

The Illinois field is the logical development of the Lima-Indiana. While the pools are chiefly near the eastern edge of the State, small reservoirs have been found in many scattered localities as far west as the Mississippi River. The field has passed its peak, but exhaustion is

delayed by the unusual number of oil strata frequently found in the same well. The oil is more easily refined than that of Lima-Indiana.

The Mid-Continent field embraces the states of Kansas and Oklahoma, together with northern and central Texas, northern Louisiana, and the new pools in Arkansas. This grouping is entirely for industrial purposes, and the field includes widely differing natural conditions. Thus the oils of Kansas and Oklahoma are obtained chiefly from rocks of Carboniferous age, while in northern and central Texas they come not only from Carboniferous but also from younger rocks.

The northern Louisiana and Arkansas pools are more closely related, and obtain oil from Tertiary and Cretaceous formations. The oil generally contains paraffin. Occasionally it is contaminated with asphalt. A few individual pools are poorer in quality, as they contain more sulphur, which interferes with refining. This Mid-Continent field was in 1921 at the top of its production, and is the dominant feature of America's oil industry, since it is connected by efficient pipe-line service with the refineries of the Eastern and Gulf coasts. Oil has been produced in Kansas for many years, especially at the northern end of the field. The old pools as they have declined have been augmented from the Augusta, Eldorado and Peabody pools farther west, where the oils were frequently found at such shallow depths that a well would be 'begun Monday, finished Saturday, and paid for in another week!' The great development began by the extension of the field into Oklahoma, where the great 'Glenn' pool justified the laying of pipe-lines connecting with those in the east, so that oil now flows 1600 miles from Oklahoma to New York and other eastern ports. Other lines connect the region to the Gulf ports, there to be refined or shipped in its crude state to population centres. Pools like the Glenn in their enormous yields have been found repeatedly in Oklahoma, and even in 1920 the finding of new pools was such a feature as to bring the total to a higher point than ever before, 105,725,000 barrels (16,793,328 metric tons). In northern and central Texas, the Burkburnett, Ranger, Eastland, and other pools have proved great producers, but have been drawn upon too heavily, and have declined rapidly.

Northern Louisiana is characterised by the Caddo pool, where high-grade refining oil is the chief product. Numerous other pools, such as the Homer, Bull Bayou, and Haynesville, are interesting in their present development and future possibilities. The wells are usually deep —2000 to 3000 feet. They are found in anticlinal domes or folds incidental to the Sabine uplift. Usually they are so hidden by quaternary cover as to make geological exploration difficult. This is especially true of the new El Dorado, which is an extension of the Louisiana conditions into Arkansas. This field, while only a year old, will add greatly to the total supply. The oil is heavy and somewhat asphaltic. The Gulf field came into importance by the discovery of oil by Capt. A. F. Lucas, near Beaumont, in south Texas. It was found at Spindle Top, a low, scarcely-discernible mound, which proved to be the top of a large dome of rock-salt. It led to the finding of many more similar domes, which appear to be related to the intersections of a great system of faults. Similar domes are productive on the adjoining coast of Louisiana. After a short period of gusher production these coast pools 'settle down' to small, but enduring, production, which has frequently been augmented by deeper drilling. New discoveries have been sufficient to keep this region very important. The oils are high in asphalt and sulphur, and the accompanying gas is rich in hydrogen sulphide. The sulphur is easily eliminated, and the refined products include fine lubricating oils. Much of the fuel oil for the Navy of the United States and for export to Europe has been furnished from the Gulf Coast.

The Rocky Mountain field formerly was limited to two small pools in Colorado, where the oil was found in crevices in shales. Now the State of Wyoming yields a large supply, chiefly from the great Salt Creek pool. Other important developments are widely scattered over the State, including the Big Muddy, Rock River, Lost Soldier, Lance Creek, Poison Spider, and Elk Basin pools. Altogether, Wyoming will long be an important oil region.

Montana yields oil from an extension of the Elk Basin, Wyoming pool, and from a development just beginning at Cat Canyon. Exploration work has also shown the probability of other significant pools in the south-eastern part of Montana.

California produces oil in great quantities. It is so far removed from Eastern competition as to be less related than Mexican oils. It produces about the same quantity of oil as does Oklahoma. It is heavy, usually asphaltic, low in gasoline, and contains significant amounts of the aromatic series of hydrocarbons. The 'West Side' field, which includes the Coalinga, Elk Hills, McKittrick, Midway, Sunset, and Maricopa pools, has been the main producer of the State. Lately the Whittier-Fullerton pool, near Los Angeles, has grown to great proportions. Still later, oil has been found at Huntington Beach, on the Pacific Coast. In Ventura County, the oldest pool in the State has lately increased in production, yielding oil rich in gasoline. The Kern River is another old pool, in Kern County, which has produced heavy asphaltic oil for fuel purposes for many years. All of the present oil production comes from the southern half of California. Exploratory effort is now directed toward finding oil in the northern counties, and in the State of Washington.

The oil formations are of recent (Tertiary) age, and probably originate in deeply buried portions of the great diatomaceous shale beds, from which it has accumulated in anticlinal structures. Much of the oil has also migrated into fine pores of shales, which are frequently very thick, and richer than the Scotch oil shales.

2. *Physical and Chemical Properties.*

The petroleums of North America differ very greatly in their physical properties. Very small quantities of oils as light in sp.gr. as 0·700 are occasionally found in the Appalachian region. At the other extreme are oils found in small quantity in the Santa Maria oil-field, in California, which are heavier than water. These heavy oils are semi-solid at 60° Fahrenheit.

They contain an exceptionally high percentage of nitrogen. It has only lately been shown that these oils contain unusually large amounts of resins, which are the cause of their high specific gravity. Between the extremes mentioned, all possible variations in specific gravity, viscosity, colour, etc., are found.

In general, the petroleums of North America consist chiefly of hydrocarbons of the paraffin, or methane, series (C_nH_{2n+2}). The hydrocarbons of other series present in the American petroleums vary in character and in quantity in different localities, these small constituents having in general been given greater prominence than they deserve, although they are frequently present in sufficient amount to characterise the oils and to distinguish one locality from another.

The oils of Pennsylvania and New York, West Virginia and eastern Ohio, are composed almost entirely of members of the paraffin series, with indications of increase in the proportions of olefines in the higher distillates. They usually contain from 2 to 4 p.c. of paraffin wax. Occasionally oils with considerable proportions of asphalt are found in Kentucky and Tennessee. The oils of western Ohio and of Indiana are characterised by organic sulphur compounds, which the researches of C. F. Mabery have shown to be chiefly thiophanes. While the percentage of sulphur in these oils is generally less than 2 p.c., the character of the compounds makes it necessary to remove them entirely by expensive processes. Sulphur and asphalt are both frequently found in the oils of Illinois, but the sulphur is in a less refractory condition, and first-class gasoline, burning oils, and lubricants are obtained from these crudes.

Many different kinds of petroleum are found in the Mid-Continent region. Usually they are free from asphalt, and contain noteworthy percentages of paraffin wax. Other oils in this region are rich in asphalt, and also contain sulphur, as in the Healdton field. The oils of northern Texas and Louisiana resemble the paraffin oils in their high yields of gasoline, kerosene, and lubricants. The Gulf Coast oils are the highest in sulphur of any found in the United States, but its elimination is simpler than with the Lima-Indiana oil. Gulf Coast oils are usually rich in asphalt, but the lubricating oils obtained from them, characterised by the hydrocarbons of the series C_nH_{2n}, have been shown by Mabery to be of exceptional value for lubricating purposes. Refineries have lately been erected to take advantage of this feature.

The Rocky Mountain oils vary within wide limits. Most of them resemble Appalachian oils. A few are rich in asphalt. A few have the highest percentage of gasoline of any commercial supplies in the United States, the gasoline running as high as 45 to 50 p.c. in individual cases. Oil at Lander, Wyoming, is viscous, because of its high percentage of asphalt.

In California, the first oils obtained, from Ventura County, were limpid oils, of brown-green colour, and contained more than the average proportion of gasoline and burning oils. But the next oils to be developed, in the Kern River field, showed the reverse. They range from 10° to 20° Baumé (1·0 to 0·9333 sp.gr.), and contain larger amounts of asphalt than any others in the United States. The great oil supply from the 'West Side' fields is intermediate in character between the Kern River and Ventura oils, yielding a slight amount of gasoline, considerable kerosene, and good lubricating oils. The lubricating oils of California are in general of high class, except that the amount of cylinder stocks is so small that cylinder oils are imported from the East. The oils of California differ from the Eastern oils also by containing considerable proportions of the higher members of the aromatic series, with practically no benzene or toluene. They probably also contain members of the naphthene series. The quantities of these are sufficient to require modifications in refining practice, with the use of fuming sulphuric acid.

3. *Well-Drilling Methods.*

Of the many methods of drilling for oil, use is made in the United States of only two: the cable type of the percussion, or churn, method, and the rotary process. The Canadian, or pole, type of the percussion method is not used in the United States. The cable method does not differ in principle from that first used in the oil industry, except by the gradual perfection of details, which became necessary when drilling wells to depths of 3000 and 4000 feet. The cable method is in general use when drilling through hard rocks, such as hard limestones, quartzite, conglomerite, and hard sandstones. The rotary system was adopted in 1900 for drilling in soft materials, on account of the success of this method in the formations of this character in southern Texas. It is now generally used in soft formations, and in California it has been developed for use even in drilling wells deeper than 4000 feet. Where occasional hard rocks are encountered in rotary drilling, a novel revolving bit, known as the Hughes-Sharp bit, has been able to do rapid work, even in quartzite.

Pumping.—Most of the wells in the United States do not flow, and must be pumped. For this purpose pumps located at the bottom of the well, and actuated by 'sucker rods,' usually of wood, though occasionally of steel, operate a simple barrel pump, by which the oil is lifted to the surface. The oil is also taken out of the well occasionally by the air lift. This process involves the blowing of a strong blast of air through a small pipe to the bottom of the well. In returning to the surface this air carries the oil. Occasionally natural gas has been applied to the same purpose where no other use was available for it. This waste has practically ceased.

When the oil arrives at the surface it is first run into wooden tanks, of 100 to 500 barrels' capacity. These when full are turned over to the agent of the pipe-line company, who gauges them and pumps them to the field-storage tanks, from which they are pumped to the refining regions. The pipe-lines are usually 8 inches in diameter, with occasional loops of 10 or 12 inches. Many of the so-called 8-inch pipe-lines have several parallel lines or loops, where it is necessary to pump the oil over considerable grades.

4. *Processes of Refining and Manufacture.*

Very little petroleum is used in the crude state, except as a fuel. Even in this case the

light oils are usually separated from the fuel oil by distillation, even when the total amount of light distillates thus 'topped' is not more than 10 p.c.

The difference in boiling-points of the constituents of petroleum is used as the general means of parting the crude oil into several classes for their various uses.

Distillation.—During the years 1920 and 1921 distillation methods have changed markedly. At present, horizontal cylindrical stills, of 1000 barrels' capacity, are the ones commonly used. These are provided with 'bottom steam and top steam.' The still, heated by the residual oils and other so-called fuel oils (that is, oils of low value in the refinery), is brought to a temperature where the gasoline content is distilled off. It is now good practice to introduce steam through perforated pipes in the bottom part of the still, and thus lower the temperature at which the distillates come off, and keep the oil water-white as long as possible. By this means a considerably greater amount of water-white kerosene is obtained. After this, top steam is introduced, to prevent the condensation of the heat vapours on the top surface of the still, and consequent cracking to dark-coloured products. Until lately it has been the practice to reduce crude petroleum, in the large stills mentioned above, to a tar, called residuum. This is then pumped into smaller 'tar stills' and distilled down to coke, with the production of some cracked 'prime white,' or 'standard white,' kerosene, and the usual array of paraffin lubricating oils. This method is still practised, but in many cases has been changed to a radically different procedure. This consists in equipping these large stills with so-called towers, in which the vapours are fractionated, and very much better separation obtained. Instead of allowing the heavier liquids which condense in the towers to run back in the stills, piping is provided by which the heavier distillates can be shunted from the tower into separate tanks. With this arrangement it is the practice to run the crude oil to coke in the original crude still. The use of steam in such distillates is on the increase. It is now possible to separate good lubricating oil 'stocks' from these first crude stills. It is the practice to separate the gasoline portion usually referred to as crude naphtha, then burning oil distillate, '300 oil,' gas oil, and the usual grades of lubricating oils. If the oil is capable of furnishing paraffin wax, this is found in the wax distillates, and separated, as described later. Next, the crude naphtha is in some cases treated with a very slight amount of sulphuric acid, in continuous treaters, and then 'sweetened' with caustic soda, and redistilled with steam, when it is ready for the market as gasoline. The gasoline must all distil off before a temperature is reached of 437°F., called the end point. Usually the distillation of crude naphtha leaves in the still a certain amount of oil which distils above 437°F. This is called naphtha still bottom, and is piped to the crude burning oil distillate, which, on similar treatment, with sulphuric acid, soda, and steam stilling, is made ready for market as kerosene. The still bottoms from this kerosene distillation are either returned to the crude stills, or turned into the gas oil tank, according to its characteristics. Very little further treatment is given to the gas oils before selling them for the purpose of enriching gas or for mixing with other fuel oils. Each crude lubricating oil is usually finished to make it stand the exact test for flash point, fire test, viscosity, etc., specified by the buyer. This usually involves distilling off a light portion in a steam still, the light portion being returned to the appropriate fraction. The last oils to distil over from the crude stills contain such paraffin wax as may be characteristic of the crude petroleum used. These oils are chilled with an ammonia ice machine to the paraffin wax obtained by filter processes. This crude wax is then remelted and run into shallow trays, containing pebbles, solidifying by chilling. The temperature is then very gradually raised, until the lighter portions are fractionally melted and run away, leaving the more solid portion of the wax. Before 'sweetening,' the oil is frequently purified by sulphuric acid, but the use of filtering media, such as fuller's earth, and various kinds of 'activated' charcoal, is becoming more common.

An improved innovation in the treatment of wax oil is that of cooling the oil with brine solution and separating the wax by supercentrifuges, which attain a speed of 40,000 revolutions per minute. The development of the continuous treatment of oils with sulphuric acid, the increased use of filtration through clays, charcoals, and silica gels, the separation of wax by the centrifuge method, and the increased use of steam in distillation, are the innovations which show the tendency of changes in refining technology.

Certain varieties of crude petroleum from the Lima region of Ohio have required special methods of eliminating sulphur, especially when this is in the form of organic sulphur compounds. A declining supply of these materials and the advent of modern methods of cracking these oils by which the sulphur is eliminated as sulphuretted hydrogen, have greatly decreased the use of such special sulphur-eliminating methods.

Large amounts of asphalt obtained from the asphaltic oils of California, Southern Texas, and Mexico are now utilised for road-making purposes. Such asphalt is merely the residuum from distilling off the light oils from these asphaltic varieties of crude petroleum.

5. *Character of Products and Utilisations.*

The names of commercial products obtained from petroleum have, of course, been almost infinitely varied, as each manufacturer has his trade names for his special products. We shall only designate the generally accepted classes of products. The first fraction commercially obtained is the 'light naphtha.' From this may be obtained by special fractioning and proper condensation :—

Cyomogene, gaseous at ordinary temperatures, but liquefiable by cold or pressure, b.p. 0°C. sp.gr. 110°B. Used in the manufacture of ice.

Rhigolene, condensable by the use of ice and salt, b.p. 18·3°C., sp.gr. 0·60 or 100° Baumè. Used as an anæsthetic for medical purposes.

Light Petroleum or *Petroleum ether* (*Sherwood oil*), b.p. 70°–90°C., sp.gr. 0·650–0·666 or 85°–80° Baumè. Used as a solvent for caoutchouc,

asphalts, and fatty oils, and for carburetting air in gas machines.

The light petroleum used by chemists for solvent purposes may be very light, 88°B., or may be as heavy as 62°B., which latter is used in certain classes of extraction.

Ligroin is another name for light petroleum.

Benzine (deodorized), sp.gr. 0·638–0·660 at 25°C. (82°–90°B.), boiling at 45°–60°C., is the light solvent described in the U.S. Pharmacopœia.

Gasoline.—This term is now broadly applied to the product used for automobiles, motor-boats, and internal-combustion engines, and because of its demand may vary widely in quality. Moreover, as gasoline is made now not only from Pennsylvania oil, but from oils like California and Mid-Continent, which are differently constituted chemically, the products will differ quite notably in physical characters. Thus a California naphtha of 66°B. gravity will evaporate at ordinary temperatures much more readily than Pennsylvania gasoline reading 80°B. or higher. Or again, a well-made 60°–63° gravity naphtha, manufactured from Mid-Continent crude, has a lower b.p. than 76° gravity naphtha made from Pennsylvania crude.

The practice of extracting very light, so-called 'casing-head,' gasoline from the natural gas obtained from oil-wells is increasing, so that 351,535,026 gallons of such gasoline were obtained in the United States in 1919. The first process employed for obtaining gasoline from natural gas was based on compressing the gas to pressures from 75 to 200 lbs. per square inch. More recently, the Saybolt process has been developed, by which the gasoline is scrubbed from the gas by passing the gas through towers containing porous material or baffle plates, over which an oil, intermediate between kerosene and gas oil, known as 'mineral seal,' is allowed to flow. The gas enters the tower at the bottom, and meets the oil flowing down from the top over the porous material. By this means it is possible to extract gasoline from natural gas containing as little as one-half gallon per thousand cubic feet. A later process is in course of development for extracting the gasoline by passing the gas through specially prepared charcoal and through silica gels.

In general, commercial gasolines are of heavier gravity than before the demand grew to its present figures.

The former method of grading gasoline by the gravity of the product has, by governmental advice, in the United States, been largely superseded by actual distillation tests. These tests prescribe a certain minimum temperature at which 5 p.c. of the gasoline shall distil off and also a maximum temperature, usually 437°F., at which the distillation flask must be empty. By this means a very greatly increased supply of gasoline has been obtained, the quality of which is fully as good for automobile use as the gasolines previously obtained, which were characterised by lower boiling-point. Inasmuch as gasoline is 'bought by the gallon and burned by the pound,' the more pounds of gasoline in the gallon the greater the number of heat units, and, hence, the greater number of miles obtained with heavier gasolines per unit of volume.

Burning Oil or *Kerosene.*—There has been little change in the characteristics of burning oils within the last few years. In spite of the adoption of electric lighting, sales of kerosene have not declined, it being merely possible for electric lighting to keep pace with the increased total of artificial light demanded with the growth of civilisation. The different burning oils are known often by special names, of which the number is legion, but they are graded by the American petroleum exporters chiefly according to the two standards of colour and fire-test, the colours ranging from pale-yellow (standard-white) to straw (prime-white), and colourless (water-white). The fire-tests to which the commercial oils are mostly brought are 110°F., 120°F., and 150°F., that of 110° going mainly to the continent of Europe and to China and Japan, and that of 120° to England.

Lubricating Oils.—In general there have been only slight changes in the character of the lubricating oils that are manufactured from petroleum. The tendency is to decrease the amount of animal and vegetable oils which are added to lubricating oils. This is now practically limited to certain cylinder oils where apparently a real advantage is obtained by compounding.

Use of greases (emulsion of solid oils with lime and other soaps of fatty acids) is increasing. Of special interest is the great use of graphite, a lubricant of the 'oildag' type. Oildag is made by grinding extremely pure artificial graphite to a fine powder, manipulating it with an astringent, and then mixing the graphite with a small amount of oil, to form a paste. When this is introduced into a lubricating oil of requisite quality, the graphite will remain suspended, and it is claimed that the addition of three-tenths of 1 p.c. of such graphite to an automobile lubricating oil results in a great improvement in the lubrication. D. T. D.

Petroleum from other Sources than America.

Towards the close of the nineteenth century the United States and Russia occupied positions of greater importance in respect of the present and prospective supplies of petroleum than is now the case, for within recent years there has been great activity in the exploration of petroliferous regions and the exploitation of other sources of supply, with the result that, although the United States furnishes considerably more than half the aggregate output, many other countries are now contributing on a scale of increasing commercial importance, and the production of petroleum has become widespread in character.

In these circumstances it is desirable to give statistics of the world's output of petroleum for 1916, the latest year for which official returns are obtainable, before proceeding to supplement the account of the petroleum industry in the United States by particulars of the corresponding industry in other countries (see top of next page).

Russia.

Probably the earliest record of native petroleum in the Russian Empire is to be found in the legendary accounts of Prometheus and

World's Production of Crude Petroleum.

Country.	1916. Metric Tons.	1916. Percentage of total.	Total production, 1857–1916. Metric Tons.	Total production, 1857–1916. Percentage of total.
United States [1]	40,102,288	65·26	522,310,554	60·46
Russia [2]	9,933,387	15·80	232,917,643	27·22
Mexico	5,308,987	8·64	21,728,995	2·52
Dutch East Indies [3]	1,820,247	2·86	21,849,705	2·50
Roumania [2]	1,432,296	2·23	18,910,174	2·16
India	1,132,152	1·84	12,011,136	1·39
Galicia	898,670	1·40	19,817,034	2·20
Japan and Formosa	399,624	0·65	4,422,230	0·51
Peru	340,086	0·55	2,579,315	0·30
Trinidad [4]	139,082	0·22	531,214	0·06
Germany [4]	140,000	0·22	2,015,974	0·23
Argentina	116,000	0·19	267,693	0·03
Egypt	54,800	0·09	234,658	0·03
Canada	26,416	0·04	3,187,626	0·37
Italy [4]	6,000	0·01	125,884	0·02
Other countries	3,333		52,933	
	61,853,368	100·00	862,962,768	100·00

of the Argonauts. Prometheus, it will be remembered, stole fire from heaven, conveying it in a hollow reed. In plain language, he produced fire by friction of the edges of a split bamboo. Being thus rendered independent of lightning-struck timber as a means of ignition of fuel, he was supposed to have defied the gods! As a penalty, he was chained to a rock in the Caucasus, a vulture devouring his liver during the day, and vomiting the result of the surfeit as a *black oil* at night. This was in the kingdom of Colchis, the western part of the province of Kutais, where exudations of such oil are frequent in the district north of Batum. Medea, daughter of the King of Colchis, was a noted sorceress, and Oleum Medeæ is one of the many names given to crude petroleum. When Jason, with the Argonauts, came to Colchis in quest of the Golden Fleece, Medea favoured him with some of this magic oil, which, by one account, rendered him immune from injury by the dragon guarding the treasure, or, by another form of the legend, put the dragon to sleep. The antiseptic action of crude petroleum, and the narcotic effect of inhaled oil-vapour, will fit with either variant of the history. It may be added that the Georgian name for the oil, zakupre, is philologically akin to the Hebrew gaphrith, applied to the mineral pitch of Mesopotamia and of the Dead Sea, and also to the gopher or cypress, whence pitch is produced by distillation. The Georgian deposits, though believed to be extensive, have remained undeveloped. Their position, close to the coast of the Black Sea, may be an element of much importance in the future.

There can be little doubt that the so-called Eternal Fires at Surakhani, on the Apsheron peninsula, have been frequented by fire-worshippers since the commencement of the Zoroastrian period, to which the date of 600 B.C. has usually been assigned, although the temple which now stands in that locality is considered to be of Hindu origin, and is probably not more than two centuries old.[1] In Gibbon's 'Decline and Fall of the Roman Empire' it is recorded that Heraclius, having, in A.D. 624, wintered in the Mogan Steppes, at the mouth of the river Kura, 70 miles south of Baku, 'signalised the zeal and revenge of a Christian Emperor. At his command, the soldiers extinguished the fire and destroyed the temple of the Magi.'

Marco Polo, writing in the thirteenth century, says, 'On the confines towards Georgine, there is a fountain from which oil springs in great abundance, inasmuch as a hundred shiploads might be taken from it at one time. This oil is not good to use with food, but 'tis good to burn, and is also used to anoint camels that have the mange. People come from vast distances to fetch it, for in all the countries round there is no other oil.'[2] With reference to this, Colonel Yule remarks, 'Though Mr. Khanikoff (the celebrated Russian traveller) points out that springs of naphtha are abundant in the vicinity of Tiflis, the mention of shiploads (in Ramusis, indeed, altered—probably by the editor—to camel-loads) and the vast quantities spoken of, point to the naphtha wells of the Baku peninsula on the Caspian. Ricold speaks of their supplying the whole country as far as Bagdad, and Barbaro speaks of their practice of anointing camels with oil.' Peter the Great, upon annexing Baku in 1723, made arrangements for the collection of the oil and its transportation up the Volga. A few years later, Baku having meanwhile been restored to Persia, attempts were made by England to establish a trade with India *viâ* the Caspian Sea, and, some complications having arisen, Mr. Jonas Hanway was deputed to proceed to Persia to investigate affairs. Upon his return Mr. Hanway published, in 1754, An Account of British Trade over the Caspian Sea, wherein the following references to petroleum occur: 'What the Guebers, or Fire-worshippers, call the Everlasting Fire, is a phenomenon of a very extraordinary nature. This object of devotion lies about ten English miles north-east by east from the City of Baku, on a dry rocky land. There are several ancient temples built with stone, supposed to have been all dedicated to fire. Amongst others is a little temple at which the Indians now worship. Here are generally forty or fifty of these poor devotees, who come on a pilgrimage from their own country. A little way from the temple is a low cleft of a rock, in which there is a horizontal gap, two feet from the ground, nearly six long, and about three broad, out of which issues a constant flame, in colour and gentleness not unlike a lamp that burns with spirits, only more pure. When the wind blows it rises sometimes eight feet high, but much lower in still weather. They do not perceive that the flame makes any

[1] Marketed production.
[2] Estimated in part.
[3] Includes British Borneo.
[4] Estimated.

[1] When the present writer visited Baku in 1884, he found this temple deserted, and the fires extinguished, but he had no difficulty in igniting the gas.

[2] The Book of Ser Marco Polo, the Venetian. Edited by Colonel Henry Yule, C.B., London, 1871.

impression on the rock. This also the Indians worship, and say it cannot be resisted, but if extinguished will rise in another place. The earth round the place, for above two miles, has this surprising property, that by taking up two or three inches of the surface and applying a live coal the part which is so uncovered immediately takes fire, almost before the coal touches the earth; the flame makes the oil hot, but does not consume it, nor affect what is near it with any degree of heat. Any quantity of this earth carried to another place does not produce this effect. Not long since eight horses were consumed by this fire, being under a roof where the surface of the ground was turned up, and by some accident took flame. If a cane or tube, even of paper, be set about two inches in the ground, confined and closed with earth below, and the top of it touched with a live coal, and blown upon, immediately a flame issues without hurting either the cane or paper, provided the edges be covered with clay; and this method they use for light in their houses, which have only the earth for the floor. Three or four of these lighted canes will boil water in a pot, and thus they dress their victuals. The flame may be extinguished in the same manner as that of spirits of wine. The ground is dry and stony, and the more stony any particular part is, the stronger and clearer is the flame; it smells sulphurous, like naphtha, but not very offensive. Lime is burnt to great perfection by means of this phenomenon, the flame communicating itself to any distance where the earth is uncovered to receive it. The stones must be laid on one another, and in three days the lime is completed. Near this place brimstone is dug, and naphtha springs are found. Baku supplies Ghilan and Mazanderan and other countries contiguous with naphtha.' Hanway adds that 'the chief place for the black or dark-grey naphtha' was 'the small island Wetoy, now uninhabited, except at such times as they take naphtha from thence.' The island thus referred to is Sviatoi or Holy Island, which lies at the extremity of the peninsula of Apsheron. Of the Wetoy naphtha Hanway says, 'The Persians load it in bulk in their wretched vessels, so that sometimes the sea is covered with it for leagues together. When the weather is thick and hazy, the springs boil up the higher, and the naphtha often takes fire on the surface of the earth, and runs in a flame into the sea in great quantities, to a distance almost incredible. In clear weather the springs do not boil up above two or three feet; in boiling over the oily substance makes so strong a consistency as by degrees to almost close the mouth of the spring. Sometimes it is quite closed, and forms hillocks that look as black as pitch, but the spring which is resisted in one place breaks out in another. Some of the springs which have not been long open form a mouth of eight or ten feet diameter. The people carry the naphtha by troughs into pits or reservoirs, drawing it off from one to another, leaving in the first reservoir the water or the heavier part with which it is mixed when it issues from the spring. It is unpleasant to the smell, and used mostly among the poorer sort of the Persians and other neighbouring people, as we use oil in lamps, or to boil their victuals; but it communicates a disagreeable taste. They find it burns best with a small admixture of ashes. As they obtain it in great abundance, every family is well supplied. They keep it at a small distance from their houses, in earthen vessels underground, to prevent any accident from fire, of which it is extremely susceptible.' Hanway also describes a 'white' variety of naphtha, collected on the peninsula of Apsheron, as 'of a much thinner consistency than black naphtha. The Russians drink it both as a cordial and medicine; but it does not intoxicate. If taken internally it is said to be good for the stone, as also for disorders of the breast, and in venereal cases and sore heads; to both the last the Persians are very subject. Externally applied, it is of great use in scorbutic pains, gouts, cramps, &c., but it must be put to the part affected only; it penetrates instantaneously into the blood, and is apt, for a short time, to produce great pain. It has also the property of spirits of wine to take out greasy spots in silks or woollens, but the remedy is worse than the disease, for it leaves an abominable odour. They say it is carried into India as a great rarity, and being prepared as a japan is the most beautiful and lasting of any that has yet been found.' A third source of petroleum mentioned by Hanway is the island of Tcheleken on the eastern side of the Caspian. Of this island, on which at the present time great activity prevails in petroleum-prospecting, Captain Woodroffe says, 'We weighed, and came in close under the east side of Naphtonia, as the Russians call it. The Persians call it Cherriken. The coast is difficult of access, being high. It contains about thirty-six families, who have twenty-eight large boats, with several wells of naphtha. The people exist entirely by piracy. To remedy this evil Nadir Shah, some years ago, offered to forgive all that was past, and to receive them into his favour, if they would come and settle about Astrabad Bay, where they might have lands and sell their naphtha to the inhabitants of that quarter. This they accepted, and carried on a brisk trade for about two years, selling their naphtha to the Persians, Turkomans, &c.; but, getting tired of this way of living, returned to their trade of piracy.'

Russia again annexed Baku in 1806, and the monopoly of producing petroleum was conferred on a merchant of the name of Mirzoeff, who held it until 1872, when the monopoly was revoked and a tax imposed.

The abolition of the monopoly had the effect of greatly increasing the production, and Mirzoeff did not long retain a position of supremacy, for in 1873 the Khalify Company struck a flowing well which yielded a large supply; and in the following year the Transcaspian Trading Company, afterwards called the Baku Petroleum Company, took the lead in the business. In 1875 Messrs. Nobel Brothers commenced the systematic production, refining and transportation of petroleum upon a large scale, and by the introduction of approved appliances for drilling and refining, as well as by the installation of a complete system of pipe-lines, tank steamers, tank barges, tank railroad waggons, and storage tanks, inaugurated a new era in the Russian petroleum industry.

For many years these operations were

confined to a few square miles in the Baku district, the producing fields including Balakhani, Sabuntchi, Romani, and Bibi-Eibat, but within this small area such prolific wells were drilled that a very large production was obtained. Thus the celebrated Droojba fountain, completed in 1883, commenced spouting at the rate of 1,600,000 to 2,000,000 gallons daily, valued at £11,000, and other wells drilled within later years have had for a time a daily yield of more than double that quantity.

In 1893 the Grozni field, which lies about 300 miles north-west of Baku, began to attract attention, and two years later it gave so productive a fountain that the outflowing oil converted a neighbouring valley into a vast lake in which large ships could have floated. From that time the progress of Grozni was rapid, and it now ranks as one of the great oil-fields of Russia.

The oil-field of Maikop, in which a large amount of English capital has already been expended in drilling operations, is situated in the Kouban territory, about 300 miles west of Grozni. The early promise of large production from moderate depth given by the completion of prolific spouting wells has not been fulfilled, but deep test-wells are being drilled. Meanwhile, however, a steady yield is being obtained from certain parts of the field. Other petroliferous lands lie still further to the north-west on the Taman Peninsula.

As already mentioned, the Island of Tcheleken, on the eastern side of the Caspian Sea, is now being actively exploited with the drill, and spouting wells have been obtained. Ozokerite is also being obtained here in commercial quantity.

Another district of much promise for future exploitation, although as yet very partially investigated, is that of the Uralsk province, to the north-east of the Caspian Sea. Here evidences of the presence of oil are reported at many points of the steppes, from the borders of Astrakhan to the foot of the Mugodjar Hills, which represent the southern extremity of the Ural Mountains. Although exploitation only began in 1911, the several companies operating had in 1914 some fifty-nine wells in yield, producing an appreciable fraction of the Russian total.

The cable system of drilling, commonly employed in the United States, which has already been described, has not found favour in Russia, although it has been used. The method adopted is, however, substantially similar, in the sense that the strata are perforated by rapidly successive blows of a steel bit, or cutting chisel, suspended from the end of an oscillating beam, but the drilling tools are attached to the beam by a string of screw-jointed iron rods, added to as the depth of the well increases, instead of being suspended by a Manilla cable, as in America. As the drilling progresses, the detritus is, from time to time, removed from the bore-hole by means of a long cylindrical vessel with a foot-valve, as in the American system. The well is also similarly lined with iron casing, but, owing to the large diameter, riveted casing is used in place of screwed artesian casing. The greater diameter of the Russian wells is due to the need for providing for the use of a bailer (valved cylinder) for raising the oil when the well does not flow, the oil containing so much sand that pumps cannot be used. To some extent the air-lift system of raising the oil has been substituted for bailing within recent years. Motive power for the drilling machinery is ordinarily supplied by a steam-engine, and it is customary to take the steam supply from a central generating station, but the internal combustion engine is also employed, and the use of electricity as a motive power is growing. The oil is transported to the refineries by means of pipe-lines, as in America, and is to some extent stored in similar iron or steel cylindrical tanks of large size, but earthen storage reservoirs are also largely used.

In the refining of the crude oil it is the practice to adopt the system of continuous distillation, which consists in causing the oil to flow through a connected series of horizontal stills heated to successively higher temperatures, each still being provided with a separate condenser, so that a series of distillates of progressively higher boiling-points is simultaneously obtained. In this respect the process of fractional distillation differs from that adopted in America. In the treatment of Baku petroleum the refiner aims at obtaining the largest yield of the ostatki, or residuum, for which there is a large sale as liquid fuel, the kerosene being a product of secondary importance, though a certain proportion of the residuum is further distilled for the manufacture of lubricating oils, as in America. The 'cracking' process, largely employed in the United States as a means of increasing the yield of kerosene and motor spirit, is not adopted in Russia, and in this respect also the procedure in the two countries differs. The yield of kerosene from the crude oil of the older Russian fields does not usually exceed 25-30 p.c., and in the manufacture of the lubricating oils there are no solid hydrocarbons to be separated in the form of paraffin wax, as in America; but oils are now being met with in the newer Russian fields which not only contain a far larger proportion of the more volatile hydrocarbons, but also a considerable percentage of solid hydrocarbons.

The crude petroleum of the Baku district has a specific gravity usually within the limits of 0·855 and 0·875. It is of dark-brown colour and not unpleasant odour. In chemical composition it differs from Pennsylvania and other United States oils in largely consisting of hydrocarbons of the C_nH_{2n} series, which belong not to the ethylene group, but to what is known as the naphthene, or $C_nH_{2n-6}+H_6$, group.

The yield of benzine from the oil of the Balakhani-Sabuntchi field is very small, but a larger proportion of this product is obtained from the Bibi-Eibat oil. The kerosene ordinarily has a specific gravity of about 0·825, which is considerably higher than that of the parallel United States product. Of residuum (ostatki), or fuel oil, with a specific gravity of about 0·912, the yield is from 50 to 60 p.c. The flash-point of this fuel oil is about 140°F., and its calorific value is 10,800 calories, or 19,440 B.T.U. The comparatively small proportion of the residuum which is subjected to further distillation for the manufacture of lubricating oils yields first an intermediate

product, known as solar oil, which is largely used as a source of gas for illuminating purposes. About 30 p.c. of the residuum is represented by a machine oil of a specific gravity of about 0·908, and of fairly high viscosity, which is an excellent lubricant for general use.

The crude petroleum of the Grozni field is of higher specific gravity than that of the Baku region, but contains a larger proportion of the more volatile constituents.

For consumption in Russia the kerosene is conveyed from the Baku refineries in bulk by tank-steamers to the mouth of the Volga, and thence by tank-barges and railway tank-waggons. For shipment abroad the kerosene was formerly transported to Batum by railway tank-waggons, but within recent years a pipe-line for the conveyance of it to the Black Sea has been in operation.

Galicia. The petroleum industry of Galicia is one of considerable antiquity, for the oldest historical records show that the oil was collected for use as cartgrease from very early times, and as a medicinal agent Galician petroleum was held in high repute, under the name of 'earth balsam,' as far back as 1506. In 1810, or between that year and 1818, oil from the Drohobycz district is said to have been distilled by Hecker and Mitis in a small refinery at Kabicza, and the product is reported to have been used for lighting the Alstettering in Prague. Refining does not, however, appear to have been generally practised until 1852, when a manufacturer of cartgrease named Schreiner took some of the liquid condensed on the cover of a vessel in which he had heated the crude oil to an apothecary of the name of Mikolasch, whose assistants, Lukasiewicz and Zeh, treated the distillate with sulphuric acid and caustic soda, and obtained a burning oil of such excellence that renewed attention was directed to the subject. In the following year Galician petroleum replaced candles for lighting the station of the Emperor Ferdinand's North Railway, and in 1854 it obtained a footing as an article of commerce in Vienna.

The Galician oil-deposits extend for a length of about 220 miles, with a width of 40 to 60 miles, in a general north-westerly and south-easterly direction along the northern slopes of the Carpathian mountains. The unexploited deposits in Bukowina and in Tranasylvnia, and the highly important and rapidly developing oil-fields of Roumania, occupying the south-eastern and southern slopes of the Southern Carpathians or Transylvanian Alps, may be regarded as an extension of the Galician deposits.

The earliest systematic exploitation of the petroliferous lands of Galicia was commenced in 1854 in the Bobrka district, between Krosno and Dukla; but the wells were merely shallow hand-dug shafts, which yielded no great quantity of oil, and it was not until many years later, when drilling by steam-power was adopted, that the production assumed commercial importance. To Messrs. Bergheim and MacGarvey the credit is due of having laid the foundation of the present Galician petroleum industry by the introduction of the Canadian system of drilling in the year 1882. This system, which differs mainly from what is known as the American system in the use of wooden rods instead of a cable for the suspension of the drilling tools, was found as suitable for Galicia as it had proved to be for Canada, and for many years the only alteration made in it was to increase the weight of the tools; but latterly the much greater depth of the wells has led to the employment of a combination of the rod system with a wire-cable system. The chief centre of the petroleum industry of Galicia is the prolific Tustanowice-Boryslaw field, which yields a very large proportion of the total output. Many of the wells here exceed 1000 metres in depth, and are costly to drill, but flowing wells are frequently obtained, and the production of these is so large that heavy expenditure in drilling is justified. The crude oil is of good quality, and yields all the usual commercial products, including paraffin wax.

The world's supplies of ozokerite are mainly obtained from the Boryslaw mines. The ozokerite deposit, which is unique in character, extends over a pear-shaped area, the richest part of which is only about 52 acres in extent, and is mined by means of shafts and drifts or galleries. It occurs in veins of varying thickness, and is mined by picks. The ozokerite is obtained partly in fragments of nearly pure material, but more largely in admixture with the matrix, from which it is separated by hand-picking or sorting, and by the use of hot water, a further yield being obtained by the use of benzine as a solvent. The crude ozokerite, which is of dark greenish-brown colour, and about as hard as beeswax, is melted, cast into blocks, and delivered to the refineries, where it is treated with Nordhausen oil of vitriol and afterwards with charcoal. The purified and partly decolorised material, which is known as ceresin, has a m.p. of 61° to 78°, and is largely employed as an adulterant of, or even as a substitute for, beeswax in the manufacture of church candles. For the production of the substance of which ordinary candles of high melting-point are made, the crude ozokerite is subjected to distillation in a current of superheated steam, when about 60 p.c. of white wax of a m.p. of 140°F. is obtained. The by-products of the distillation consist of light oils and a semi-solid substance similar to vaseline, which, after purification, has been used by French perfumers as a substitute for lard in the process of *enfleurage*. The residue in the stills consists of a hard, black, waxy substance, which when incorporated with indiarubber and subjected to vulcanisation, yields the product termed *okonite*, used in coating electrical cables. Okonite is not only a good insulator, but is remarkably flexible and tough. From the residue a 'heel-ball,' employed to impart a black polished surface to the heels and soles of boots, and to the leather-work of harness, is also made (*v.* OZOKERITE).

Hungary. The oil-fields of Hungary geologically resemble those of Galicia, but the petroliferous area on the Hungarian side of the Carpathian range is comparatively narrow, and has not as yet assumed any great industrial importance.

Roumania.

As already stated, the petroliferous region of Roumania may be regarded as an extension

of that of Galicia; it is also, doubtless, connected under the sea with that of the Caucasus. The Roumanian deposits may be traced by the outcrop from the Galician frontier to the Iron Gates, a distance of about 400 miles, and the width of the belt is from 15 to 20 miles.

The use of the 'liquid bitumen' of Roumania as a medicine, as an illuminating agent, and as a lubricant, was mentioned by the traveller Raicevich in 1750, but the existence of numerous pits and timbered hand-dug shafts of great age attests the fact that petroleum was systematically collected in the country long before that date. For many years after the introduction of drilling by steam-power in Galicia the petroleum of Roumania was still obtained in this primitive fashion, and the development of the industry was retarded, but similar methods are now adopted in both countries.

The expansion of the industry has been rapid, and bids fair to outstrip that of the corresponding industry in Galicia. The principal producing territories are in the districts of Prahova, Dimbovitza, Bacau, and Buzeu, and of these the first-named has hitherto been the most important.

The crude oil is of excellent quality, and in respect of the yield of the more volatile products occupies a position midway between those of Pennsylvania and Baku oils. The manufacture of fuel oil from the Roumanian crude petroleum is very largely carried on, although the residuum is also converted into lubricating oils to a considerable extent.

Sumatra, Borneo, and Java.[1]

Sumatra. The development of the oil-fields of Sumatra dates from 1885, when a flowing well was completed on a concession, granted two years previously, in Langkat, North Sumatra. In 1890 the Royal Dutch Company was formed to exploit another concession of oil-bearing lands in Langkat, and this company, besides drilling a number of wells during the ensuing five or six years, erected a refinery on the Bay of Aru, and laid a pipe-line to convey the crude oil from the wells to the refinery. The company also acquired and worked concessions in other districts, including Perlak, in the Atchin Residency, where highly productive spouting wells were drilled, and Palembang, South Sumatra. In 1897 the Sumatra Palembang Petroleum Company was formed, and this company in the course of the next few years obtained a large yield in the Palembang district of oil of low specific gravity (0·765 to 0·775), for the transport of which a pipe-line was laid to a refinery erected on the river Lalang. In the same year (1897) a third company, the Moeara Enim Company, was formed, to work concessions on the River Enim and elsewhere in Palembang and drilled a large number of wells, many of which were 'spouters' yielding from 400 to 800 tons daily of oil of sp.gr. 0·792. This company's refinery was built on the Musi, 3 miles below the town of Palembang, and the distillation of the crude oil was conducted on the continuous principle. In 1901 a fifth company, the Moesi Ilir Company, was added to the list, and commenced work on lands situated on the right bank of the Musi. The oil obtained here from spouting wells had a sp.gr. of 0·812 to 0·889. The company laid a pipe-line to Palembang, where a refinery was built. The prominent feature of the Sumatra petroleum is the large percentage of spirit yielded on distillation. This spirit has become a very important article of commerce, and its importation into Great Britain has been of the greatest service to the automobile industry, as the supplies of motor spirit would otherwise have been inadequate to meet the rapidly growing demand.

Borneo. The pioneers in petroleum development in Borneo were the Shell Transport and Trading Company, whose properties were transferred to the Nederlandsch-Indische Industrie en Handel Maatschappij. The territory over which the company acquired exploitation rights is situated on the southern half of the east coast of Borneo, and has an area of 500 or 600 square miles. It is bounded on the north-east by the Kutei or Mahakkam River, and it extends towards the south to Balik Papan Bay, but it embraces also a strip of land on the south of the bay. Drilling operations were commenced in December, 1896, but were not actively carried on until a year or two later. The company has drilled a large number of wells, of which the maximum depth is about 1500 feet, and many of these have been flowing wells yielding abundantly. The crude oil at first obtained at shallow depth was an asphalt-base petroleum of high specific gravity, but subsequently a lighter oil of the same character was obtained at greater depth, and still later a paraffin-base oil of high commercial value was found. The company's refinery is situated on the northern shore of Balik Papan Bay. The asphalt-base petroleum of Borneo gives a large yield of excellent fuel oil, and from the paraffin-base petroleum all the usual commercial products, including paraffin wax, are obtained.

Java. The petroleum industry of Java owes its inception to the enterprise of the brothers Stoop, whose interests were acquired by the Dordtsche Petroleum Maatschappij; since the year 1886 the industry has been rapidly progressive, and now occupies an important position. The chief producing territory is situated due south and south-west of the town of Surabaya, but there are also prolific deposits in the residency of Rembang. The depth of the wells range from 500 to 800 feet, and the drilling is chiefly done by the water-flush system. The average production of the wells is not large, but the yield is satisfactorily maintained. The crude oil has a sp.gr. of 0·825 to 0·916, and it yields a large proportion of solid hydrocarbons (paraffin) of unusually high melting-point.

The following table shows the production of petroleum in the Dutch East Indies during 1918, 1919, and 1920 in metric tons.

	1918	1919	1920
Sumatra .	519,989	521,756	536,482
Java and Madura	241,211	258,655	352,474
Dutch Borneo .	999,426	1,372,140	1,455,227
Coram Island .	3,574	7,311	21,137
Total	1,764,201	2,159,862	2,365,320

[1] The Bataafsche Petroleum Maatschappij, of the Hague, now own or control all the petroleum production in the Dutch East Indies.

British India.

Burma. At the end of the eighteenth century Major Symes described the petroleum wells 5 miles east of Yenangyaung, on the Irrawadi, as supplying 'the whole Empire and many parts of India with that useful product.' At that time the oil was obtained by the natives from comparatively shallow hand-dug wells, but since 1891 drilling operations have been actively conducted in this and other districts by the Burmah Oil Company, Ltd., a British organisation which was the pioneer in the present petroleum industry of Burma. The principal yield is obtained from the Khodoung field, immediately adjoining the areas on which the native wells were dug; but oil is also found at Singu and at Yenangyat, respectively about 25 miles nearer to, and 25 miles further from, Rangoon. The Khodoung (Yenangyaung) crude oil has a sp.gr. ranging from 0·737 to 0·899, and contains so large a proportion of solid hydrocarbons that it solidifies in cool weather. The Singu oil has a sp.gr. ranging from 0·731 to 0·904, and the Yenangyat oil ranging from 0·770 to 0·890. The wells are drilled by the American system. Formerly the crude oil was conveyed by bulk-barges on the Irrawadi to the refineries at Rangoon, but the Burmah Oil Company has completed a pipe-line 275 miles in length from the fields to the refineries. The company is under contract to supply the British Admiralty with oil fuel for the Navy, and has expended a large sum of money in making provision for this.

Assam. The Assam Oil Company, Ltd., has acquired the petroleum interests of the Assam Railways and Trading Company, Ltd., and the Assam Oil Syndicate, Ltd., and is continuing the work of development carried on by those companies in the Digboi field with uniformly successful results. The company has a refinery where all the usual commercial products, including paraffin wax, are manufactured.

Mexico.

The Mexican Eagle Oil Company, Ltd., own large areas of proved petroliferous lands, and three fields are at present being exploited at Tanguijo, Tierra Amarilla, and Potrero del Llano, in Northern Vera Cruz. Fuel oil from these fields is now being supplied to the Mexican Railway, the Tehuantepec National Railway, and various steamship companies, and the crude oil is also shipped to the company's refinery at Minatitlan. The company has recently acquired the oil interest of the firm of S. Pearson and Son, Ltd., who for some years have systematically explored the Isthmus region, where they have several hundred thousand acres of petroliferous lands. Several other companies are also taking part in the development of the Mexican petroleum industry.

An illustration of the difficulties and disappointments met with in the exploitation of oil lands is furnished by the following particulars of a well drilled at Dos Bocas in 1908. This well had reached a depth of 1824 feet, when a petroliferous formation charged with oil under immense pressure was suddenly and unexpectedly penetrated. In less than twenty minutes the ground round the well began to tremble and fissures appeared, some at a distance of as much as 250 feet from the well, from which oil and gas were discharged. One of these fissures extended under the boiler, and the gas was ignited. The well burned for 58 days, during which time the oil consumed was estimated to have amounted to 3,000,000 barrels. The flame reached a height of nearly 1500 feet, and at the broadest part had a diameter of nearly 500 feet. So bright was the light emitted that a newspaper was read by it at a distance of 11 miles. In addition to oil and gas, the well discharged immense quantities of water, at times at the estimated rate of 1,500,000 barrels a day, and with the liquid about 2,000,000 tons of solid matter was ejected, a crater being thus formed which ultimately had an area of 117,600 square metres. The fire was eventually extinguished by pumping sand into the crater with centrifugal pumps.

The output of petroleum in Mexico is rapidly increasing, and that country is now third in rank among the oil-producing countries of the world.

Japan.

The Japanese oil-fields extend from the eastern shore of Saghalin in the north, through the western part of the highlands of Hokkaido, and along the coast of the Sea of Japan, and thence, traversing the provinces of Mutsu, Ugo, Utzen, Echigo, and Shinano, reach to the coast of the Pacific Ocean in the province of Totomi in the south. The chief centre of the industry is in the province of Echigo, which produces about 99 p.c. of the total output of petroleum in Japan. The usual depth of the wells is from 600 to 1200 feet, and the American system of drilling is employed.

Formosa.

Oil indications extend over 400 miles in length, and three fields were in operation in 1910, viz., Shuikkoko in Shinchikucho, Senshiuryo in Tarnancho, and Rokujuker in Kagicho.

Germany.

Petroleum is found at Wietze, Steinfördt, Oelheim, and elsewhere in the kingdom of Hanover; at Lobsann, Pechelbronn, Schwabweiler, and elsewhere in the neighbourhood of Hagenau; and in the Tegernsee district in Bavaria. The crude oil of the Wietze-Steinförde district has a sp.gr. of 0·890 to 0·930. The sp.gr. of the Hagenau oil is 0·873, and that of the Tegernsee oil is 0·812.

Peru.

The petroliferous region of Peru extends about 250 miles in a northerly and southerly direction between the town of Tumbez, on the Gulf of Guayaquil, and Point Aguja, and about 150 miles east and west, from the Pacific coast to the slopes of the Andes. The northern fields, which are in the province of Tumbez, stretch from the Zarumilla River, which divides Peru from Ecuador, to the Mancora gully. The central fields comprise a part of the province

of Paita, and extend from the Mancora gully to the south of the Silla de Paita and Foca point. The southern fields are situated in the province of Piura. The petroleum found in the hacienda La Mina Brea and Pariñas, which lies in the central portion of the petroliferous zone, was utilised by the Incas for centuries, and in the time of Pizarro it was collected in trenches and converted, by boiling it down, into a pitch of excellent quality, employed to line the porous earthen jars in which the Peruvians kept and transported their fermented liquors. In 1867, Mr. Prentice, a Pennsylvanian petroleum producer, commenced drilling wells in the Zorritos field, at the northern end of the belt, and subsequently disposed of the property to the Faustine G. Piaggio Petroleum Company. The crude oil has a sp.gr. of 0·810 to 0·840, and is rich in the more volatile hydrocarbons. In 1888 the hacienda La Mina Brea and Pariñas was acquired by Dr. Tweddle, and the London and Pacific Petroleum Company was formed. The area of the property is 600 square miles. The crude oil has a sp.gr. of 0·834 to 0·848, and yields as much as 18 p.c. of benzine. The Lobitos Oilfields, Ltd., is a British company, formed in 1908 to acquire the properties of the Peruvian Petroleum Syndicate, Ltd. The company's Lobitos property comprises an area of about 25 square miles on which a large number of productive wells have been drilled. The company also has drilling rights on a further 4560 acres in the Punta Restin oil-field, about 13 miles north of Lobitos.

Canada.

Canadian petroleum has been obtained hitherto only in the province of Ontario, although it occurs in other parts of the dominion. The petroliferous region of Ontario has an area of about 100 miles by 50 miles, but the developed territory is mainly confined to a belt 16 miles by 2 miles, situated about 16 miles east of Sarnia and extending nearly parallel with the St. Clair River. The sinking of wells in the Enniskillen district began in 1861, and the petroleum industry in Canada is, therefore, almost equal in age to that of the United States. Although many of the Canadian wells have yielded largely at first, their output has in most instances quickly diminished, and the production is mainly obtained from a large number of wells yielding only a few gallons each daily. Natural gas is also found in Ontario, and is utilised as a source of light and heat. The largest area over which petroleum indications occur in Canada lies in the region of the Athabasca and Mackenzie rivers, in the north-west part of the dominion, where immense deposits occur of so-called 'tar sands,' a fine-grained sandstone, saturated with inspissated petroleum. It has been estimated that the bituminous sands 'in sight' amount to 28·4 cubic miles, and that they contain 6·5 cubic miles, or 4,700,000,000 tons, of bitumen.

New Brunswick. The Maritime Oilfields Company, Ltd., are carrying out drilling operations under a concession, of an exceptionally favourable character, granted by royal charter in 1900, which gave the right to search for oil and gas over an area of 18,000 square miles and to select 10,000 square miles (more than one-third of the area of the province). The area selected is situated in the counties of Westmoreland, Albert, King's, Queen's, Sunbury, Kent, Northumberland, Gloucester, Restigouche, and a portion of York, and is traversed by several anticlinals, on one of which, in Westmoreland county, wells have been drilled successfully, a large yield of natural gas, in addition to oil, having been obtained. The crude petroleum is of excellent quality, with a paraffin base, and yields, in addition to 34 p.c. of kerosene, a fuel oil of high calorific value, containing only 0·14 p.c. of sulphur.

Italy.

The collection of the petroleum of Miano di Medesano was the subject of a concession granted by the Ducal Chamber in 1400, and the celebrated petroleum of Modena, at one time largely used for medicinal purposes, for lighting, and in the preparation of varnishes and paints, was discovered in 1640 by Ariosto. The petroleum of Montechino was apparently not known prior to the commencement of the eighteenth century, whilst the deposits of Ozzano and Rico di Fornovo did not attract attention until early in the nineteenth century, and those of Neviano de' Rossi, Salsomaggiore, and Lesignano de' Bagni were found still later. Petroleum from the wells of Amiano, on the Taro, was used for lighting the cities of Genoa, Parma, and Borgo San Donnino as early as 1802. The districts in Italy in which petroleum is found in commercial quantities are (1) the zone of Emilia; (2) the valley of the Pescara, in the province of Chieti; and (3) the valley of the Liri, near San Giovanni Incarico, about midway between Rome and Naples. The zone of Emilia occupies the southern parts of the provinces of Piacenza, Parma, Modena, and Bologna. Some of the Italian crude petroleum has a specific gravity as low as 0·805, and is of amber colour, but unfortunately the quantity hitherto obtained has been small.

Other sources of supply.

In addition to the sources specified in the tabular statement of production, and some others incidentally described in the preceding account, there are several potentially important petroleum-producing countries to which reference should be made.

Persia.

The occurrence of petroleum in Persia has been mentioned by travellers from very early times, and its collection from the pits of Kir ab ur Susiana (Kirab), 57 miles north-west of Shuster, was fully described by Herodotus. The petroleum deposits extend in a general south-easterly direction, from the Turco-Persian frontier, about 100 miles north of Bagdad, to the Persian Gulf. In the course of surveys conducted a few years ago, specially favourable indications were found in two districts, one at Zohab, in lat, 34° 18′ N., long. 45° 55′ E., and the other near Shuster and Ahwaz, on the Karun River, at the head of the Persian Gulf. In 1903–4 two wells were drilled at Tchiah Sourkh,

near Kasr-i-Shirin, in the Zohab district, by Mr. W. K. D'Arcy, under a unique concession granted by the Shah, giving petroleum rights over the whole Persian Empire, with the exception of certain provinces on the Caspian Sea. One of these wells began flowing at a depth of 800 feet, and the other, at a greater distance from the crest of the anticlinal, reached oil at 2100 feet. The crude petroleum had a sp.gr. of 0·815, and was of exceptionally high quality. Subsequently the Burmah Oil Company, Ltd., became associated with Dr. D'Arcy in the conduct of the development, and drilled several highly productive wells in the second of the two districts referred to. In 1909 the Anglo-Persian Oil Company, Ltd., was formed to take over the concession, and has actively continued the work. The company has constructed a refinery and laid a pipe-line. It may here be mentioned that the Persian petroleum deposits extend into Turkey, and that very promising indications are met with in Mesopotamia.

Egypt.

The oil deposits of the Red Sea have been known from time immemorial, but attention was specially directed to them during the latter part of the last century by the successful results of the exploratory work carried out by de Bay at Jebel-Zeit, about 160 miles from Suez, and Jemsah, 13 miles south of Jebel-Zeit. Jebel-Zeit, near the mouth of the Gulf of Suez, was the *Mons Petrolius* of the Roman geographers, the Arabic and Latin names both signifying Hill of Oil. Copious recent formation of oil in the coral reefs here led to abortive drilling, though some oil was found, and perseverance at Jemsah and Hurgada, some distance southward, has been rewarded with rich yield. There are reported to be extensive emanations in the Farsan Islands, off the Arabian coast of the Red Sea, about 17° N. latitude. In 1905 the Egyptian Petroleum Company, Ltd., acquired a concession over a large area at Jemsah. In 1907 the Egyptian Oil Trust, Ltd., took over the concession, and drilled a number of highly productive wells. On a portion of the area the work has been continued by the Red Sea Oilfields, Ltd., which was formed in 1910. The Anglo-Egyptian Oilfields, Ltd., the management of which is vested in the Anglo-Saxon Petroleum Company, Ltd., has recently acquired the licences and assets of the Egyptian Oil Trust, Ltd., with a view to the active development of the field, and shipments of the crude oil have already been made. Drilling operations are also being conducted by the Sinai Petroleum Syndicate, Ltd., on the Sinai Peninsula.

Trinidad.

The 'Pitch Lake' of Trinidad, which is the most important, if not the largest, deposit of solid or semi-solid bitumen, was visited in 1595 by Sir Walter Raleigh, who reported that he saw there 'that abundance of stone pitch that all the ships in the world might be laden from thence.' The area of the deposit is about 100 acres, and on the basis of an average depth of 20 feet, the quantity of the material obtainable has been estimated at over 3,000,000 tons. Gesner states, in his Treatise on Coal, Petroleum, &c. (New York, 1861), that it was from Trinidad asphalt that he first prepared kerosene.

Petroleum apparently occurs over a great part of the southern half of the island. The first important concession of oil-bearing territory was granted some years ago, on the initiative of Mr. Randolph Rust. It embraces an area of more than 50 square miles at Guayaguayare in the south-eastern corner of the island. Although the early drilling operations were attended with success, very little progress was made in the work of development until the concession passed into the hands of the General Petroleum Properties of Trinidad, Ltd. Among a large number of other companies formed to participate in the exploration and exploitation of the oil lands of Trinidad, one of the most important was Trinidad Oilfields, Ltd., which acquired the rights over areas in the Guapo and La Brea districts on which successful results had already been obtained by the Trinidad Petroleum Company, Ltd. It is, however, in the neighbourhood of the Pitch Lake that the greatest progress has been made. Here, through the enterprise of the American concessionaires of the lake and their associates, a number of prolific wells have been drilled, a refinery has been built, and the first shipment of the oil was made in the spring of 1911. The production of crude oil reached a total of 397,143 metric tons in 1919. At the present time, several fields are yielding, the most important being at Tabaquite, near the Central Range, where a crude oil rich in petroleum spirit and solid paraffin is obtained by Trinidad Central Oilfields, Ltd., the properties south of the Pitch Lake operated by Trinidad Leaseholds, Ltd., and Apex Oilfields, Ltd., and the Barrackpore field, owned by Trinidad Leaseholds, Ltd. In the last few years Trinidad has made great progress. The largest refinery in the island is at Pointe-a-Pierre, on the Gulf of Paria; the crude oil is supplied by a six-inch pipe-line 26 miles in length. Large quantities of oil fuel are produced here by Trinidad Leaseholds, Ltd., and supplied to the Admiralty, and a considerable trade in bunker fuel has been developed.

British Guiana.

There were in existence on December 31, 1917, forty-two licences to explore and two licences to prospect for mineral oil over areas in the North-Western and Pomeroon districts. Favourable indications of the presence of petroleum have been observed in the region of the River Waini, and preliminary drilling operations have been undertaken. No definite results have been recorded up to the end of the year according to the latest Colonial Office report.

Barbados.

The crude petroleum of Barbados, under the name of 'Barbados tar,' was formerly an article of commerce, and occupied an important place as a medicinal agent. It was obtained from a group of hand-dug shafts known as the Lloyd wells, in the Scotland district of the island. Drilling has been conducted in this district by the West Indian Oil Syndicate, Ltd., and subsequently by the West Indian Petroleum Company, Ltd., but only small quantities of oil have been met with.

Venezuela.

The petroleum deposits of Venezuela resemble those of Trinidad, and will probably become of great commercial importance. They occur in every province along the Caribbean coast, and extend far inland. In Bermudez there is a pitch-lake far exceeding, at least in superficial area, that of Trinidad, and the mineral is much purer.

Colombia.

Petroleum is abundantly in evidence as natural exudations on the Gulf of Darien, one spring yielding, it is said, enough oil to charge a 6-inch pipe. The phenomena range for some miles inland, and along the coast north-eastwards to the Magdalena River, up the valley of which they extend more or less continuously to near Bogota, and also on the eastern flank of the Andes, on some of the tributaries of the Orinoco.

Ecuador.

The existence of petroleum in the Santa Elena district, about 64 miles west by south of the port of Guayaquil, has been known for more than two centuries, and the oil has from very early times been collected in a primitive fashion for local use.

Argentina.

Traces of petroleum occur in many parts of the Argentine Republic, but the chief interest centres at Comodoro Rivadavia, on the coast at 46° S. lat. It is believed that the deposits extend, probably with barren intervals, from the small area at present under exploitation to the Straits of Magellan at Punta Arenas.

Oil-bearing strata of Secondary age occur in the Salta-Juguy region bordering upon Bolivia, into which they extend, but little or no development has been effected in the area of several thousand square miles.

The production from the Comodoro Rivadavia field in 1916 was 129,780 cubic metres, and there were twenty-two producing wells on December 31 of that year.

Bolivia.

Traces of oil occur in a belt through the provinces of Tarija, Sucre, and Santa Cruz, from the Argentine frontier at Yacuiva to the Madre de Dios tributary of the Madeira river. Exploratory drilling commenced in 1915. Extensive petroleum deposits are also recorded in the La Paz province, and traces in that of El Beni.

Honduras.

Petroliferous limestone outcrops for a considerable distance on the Guare mountains in Camayagua department.

Costa Rica.

Near Uscari on the Amei, Limon Province, oil seepages are numerous, and test-drilling was in progress in 1916.

Guatemala.

Indications of oil are reported in the departments of Huehuetenango, San Marcos, Quiche Alta Verapaz, and Izabal.

Chile.

In the north-west part of Tierra del Fuego, inflammable gas and exudations of oil are recorded on the Nunas river, near Punta Arenas; on the Tres Puentes river, near Cape Bogueron; on the Tres Brazos river; at Quenias Malas, Peckel Harbour, and Otway Gulf.

Morocco, Algeria, Tunis.

A belt of oil-bearing rocks extends from the Atlantic coast about Rbat and El Araish to the Mediterranean south of the city of Tunis. The Moroccan part has not been explored, but oil is reported to exist at places. In Oran a fair yield is obtained in the Tliouanet and Ain Zeft fields. In Constantine there are at present only anticipations of ultimate success near St. Amand, and in Tunis around Testour.

Madagascar.

Traces of oil have been reported as found in several parts of Madagascar, and a certain amount of drilling has been effected, but without resulting in important yield. The productive rocks constitute a belt along the western coast attaining in places a width of 120 miles. The most promising area is in the Betsiriny valley, Ankavandra district, Sakalava, between parallels 18° and 19° S. lat.

West Africa.

Traces of oil have been found, but no important yield, at Tachinta in the Appolonia district, and Cammenda in Elmina. The viscid pitch of the Ijebu district of Nigeria has not proved of commercial value, and the oils of the Cameroons, of the French Congo (Fernand Vaz, Nguni, Ogowai) and of Angola (Dande) are awaiting exploitation, if, indeed, they are true oils, and not merely exudations from bituminous rocks under the heat of the tropical sun.

Newfoundland.

The existence of petroleum on the west coast of Newfoundland has been known for about a century, for it was in 1812 that Mr. Parsons, after whom Parsons' Pond is named, used the crude oil of this district as a cure for rheumatism. Drilling operations are now being conducted at Parsons' Pond.

Alaska.

Several wells have been drilled in the neighbourhood of Katalla and excellent results obtained, in respect alike of the abundance of yield and of the quality of the oil. The producing territory has been acquired by the Amalgamated Development Company, an organisation in which Canadian capitalists are largely interested.

New Zealand.

The principal indications occur (1) in the Taranaki district on the west coast of the island at New Plymouth and on the adjacent Sugar Loaves Islands; (2) on the east coast along a belt of country extending from Horoera Point, near the East Cape, to the Okahuatin

Block, 30 miles west of Gisborne (Poverty Bay); and (3) at Kotuku, near Lake Brunner, South Island. Wells drilled at New Plymouth have yielded petroleum of excellent quality, with a sp.gr. of 0·840, and containing a large proportion of solid hydrocarbons. The exploratory drilling carried out many years previously in the Poverty Bay district was not attended with success, but as the result of further recent study of the geological conditions, it is hoped that both here and in the Taranaki district a large output may eventually be obtained.

The New Zealand Government has paid a company upwards of £100,000 for the production of the first million gallons of petroleum, and is prepared to assist further in the development of the oil-fields of the Dominion.

Papua.

The occurrence of traces of petroleum in the Dutch portion of New Guinea, reported in 1905 and 1911, seems to have met with no further attention, and probably merits none. In 1912, more important discoveries were made in British Papua, and are now under experimental test with the drill on the Vailala river, 145° 30′ E. long., some 30 miles inland.

The Testing of Crude Petroleum and of Petroleum Products.

1. *Crude petroleum.*

The examination of crude petroleum which the chemist is called upon to conduct in the laboratory for commercial purposes usually includes the estimation of water and sediment, the ascertaining of the specific gravity, flashing-point, setting-point, and viscosity, and the determination of the percentage and character of the products yielded on fractional distillation. The test recommended by Engler gives most useful information in regard to the commercial value of a sample of crude petroleum. It consists in carefully distilling the oil in a Wurtz flask, and noting the percentages of distillate obtained below 150°C. and either 300°C. if the hydrocarbons present are mainly those of the methane series, or 285°C. if they are principally naphthenes, the first fraction consisting of benzine and the second of kerosene.

The natural lubricating oils (crude petroleums) of Pennsylvania, Ohio, West Virginia, and Kentucky have been classified by the West Virginia Transportation Company according to specific gravity, and subjected to the following test :—

'In receiving and making delivery of oils shipped by the company, the water and sediment contained therein shall be determined by mixing an average sample with an equal quantity of benzine,[1] and subjecting the mixture to 120°F. in a graduated glass vessel for not less than six hours, after which the mixture cools and settles not less than two hours for light grades, three hours for A grade, four hours for B grade, six hours for C grade, eight hours for D grade, and eighteen hours for heavier grades.' The grades are as follows :—

A. 37·1° Baumé (about 0·838 sp.gr.) and lighter.

B. 33° to 37°B. (0·859 to 0·838 sp.gr.).
C. 31·6° to 32·9°B. (0·867 to 0·859 sp.gr.).
D. 30·6° to 31·5°B. (0·872 to 0·867 sp.gr.).
E. 29·6° to 30·5°B. (0·877 to 0·872 sp.gr.).
F. 28·6° to 29·5°B. (0·883 to 0·877 sp.gr.).
G. 28·5°B. (0·883 sp.gr.) and heavier.

Ordinary crude petroleum, from which kerosene and the other usual commercial products are manufactured, is in the United States required to conform to the following rule of the New York Produce Exchange, except in regard to specific gravity, as to which the restriction has been relaxed, in consequence of the fact that much of the crude petroleum now obtained has a specific gravity Baumé below 43° :—

'Crude petroleum shall be understood to be *pure natural oil*, neither steamed nor treated, free from water, sediment, or any other adulteration, of the gravity of 43° to 48°B. (0·809 to 0·786 sp.gr.).'

In order to determine whether the petroleum is a 'pure natural oil' a sample is subjected to fractional distillation, each fraction being one-tenth of the crude oil by volume, and the specific gravity of the several distillates is determined. The following results, obtained in the examination of two typical samples, indicate the form of the certificate handed to the buyer :

Oil from Parker District. Gravity 46° *Baumé.*

1st product	72°B.	6th product	46°B.
2nd ,,	62°B.	7th ,,	42°B.
3rd ,,	57°B.	8th ,,	41°B.
4th ,,	53°B.	9th ,,	42°B.
5th ,,	49°B.		

Oil from Bradford District. Gravity 43° *Baumé.*

1st product	71°B.	6th product	41°B.
2nd ,,	60°B.	7th ,,	40°B.
3rd ,,	54°B.	8th ,,	41°B.
4th ,,	49°B.	9th ,,	42°B.
5th ,,	45°B.		

The regular gradation in the specific gravities of the fractions exhibited in the foregoing certificates is taken to be a satisfactory indication that the oil is a natural product.

The examination of a sample of crude petroleum with the object of ascertaining the percentage of commercial products obtainable is not always an easy operation, especially when the quantity available is small. The writer is accustomed to conduct the fractional distillation in a glass retort embedded in sand, and to compare the results obtained with those furnished by samples of crude petroleum the yield of products from which on the commercial scale is known, but even in these circumstances some experience is needed in certain cases. The difficulties encountered arise from the circumstances that in practice in the United States some of the intermediate hydrocarbons are 'cracked,' and thus converted into kerosene to a larger extent than usually occurs when the distillation is conducted in a small retort in the laboratory, and that, on the other hand, the heavy hydrocarbons

[1] In the case of the more viscous descriptions of petroleum, the writer finds that further dilution is desirable. The *diluent* used should be previously saturated with water. Kerosene is more suitable than benzine for the dilution of very asphaltic crude oils.

composing the lubricating oil are less 'cracked' when properly distilled with the aid of steam on the large scale than when distilled on the small scale. The determination of the percentage of solid hydrocarbons is also attended with considerable difficulties when the quantity of material operated upon is small. In every case the aim should be to reproduce as far as possible the condition of practical working.

2. *Petroleum spirit.*

In the testing of petroleum spirit, including petrol, gasoline, benzine, &c., it is usual to determine the specific gravity and range of boiling-points, and it is generally desirable to make a fractional distillation of the sample in order to ascertain the percentage boiling below a series of temperatures increasing by regular intervals. 100 c.c. should be distilled from a Wurtz flask which is supported on a sand dish and has the following dimensions :—

Bulb $2\frac{3}{4}$ ins. in diameter; neck $\frac{3}{4}$ ins. in diameter, $5\frac{3}{4}$ ins. long; exit tube $2\frac{1}{2}$ ins. above shoulder. The tube of the Liebig condenser employed is 24 ins. long. The thermometer having been adjusted with its bulb at first just immersed in the liquid, is gradually raised, as soon as ebullition becomes active, so that its bulb is slightly below the rising level of the vapour (which can be seen with a strong illumination). The temperature at which the first drop falls from the end of the exit tube of the flask is taken as the initial boiling-point of the sample. The percentages collected in a 100 c.c. measure glass at different thermometer-readings are recorded, together with the final boiling-point, or temperature at which the flask becomes dry. Of late some variations of the distillation test have been put forward to overcome what is termed 'masking effect,' obtained in a distillation of such a complex mixture of compounds as petroleum spirit.

In the opinion of the writer, which has not been formed without a great deal of experimental work in the laboratory, the 'masking effect' referred to, that is to say, the retarding effect on the evaporation of the more volatile hydrocarbons in the description of apparatus mentioned above, is not a disadvantage. A commercial test, to be of service, must be expeditious and simple, and yet capable of furnishing concordant results in the hands of different operators, and these results should have some bearing on the conditions of use to which the product will be subjected in the carburettor. If, then, a petrol has only a very small quantity of low-boiling constituents, and these are 'held' by the less volatile portion of the product so that their volatility in the carburettor is reduced, obviously the effect on the hydrocarbons of higher boiling-point is to increase their volatility, and a test must take into account the respective retardation and acceleration of evaporation of the components. Thus it will be seen that complete fractionation is unnecessary.

In the test described, it will be observed that the thermometer is raised with the vapour at the commencement of the distillation, and the temperature recorded is the actual temperature of the vapour This temperature will be increased in proportion with the masking effect, and the placing of the cold thermometer at the exit tube does not avoid this occurrence, but gives a temperature reading lower than that of the vapour, and which may even vary considerably under different atmospheric temperatures with the same sample of petroleum spirit.

Deodorised petroleum spirit should have no disagreeable odour either in bulk or when evaporated on the hand. A small quantity evaporated in a basin over the water-bath should leave no oily residue. When petroleum spirit is used as a turpentine-substitute in paints it is important that it should contain no deleterious sulphur compounds. For the detection of these the sample may be boiled for a few minutes with alcohol and a few drops of ammonia, and silver nitrate solution then added, when there should be no brown coloration.

The presence of sulphuric acid may be detected by agitating the spirit with warm water, separating the water (which should exhibit no acid reaction), and adding to it a few drops of barium chloride solution.

3. *Kerosene.*

For ordinary commercial purposes the only characteristics which are noted in the examination of kerosene are the colour, the odour, the specific gravity, and the flashing-point or fire-test. In certain cases, however, special tests are applied with the object of ascertaining whether the oil is of satisfactory burning quality, is of natural composition, has been properly treated with acid, has been sufficiently washed, and is free from sulphuric acid, sulphonates, and sulphur in other forms.

(*a*) *Colour.*—Formerly it was the practice to estimate the colour of a sample by comparing it with that of a standard sample, the two oils being placed in bottles of the same size. Such a method did not, however, admit of an accurate comparison being made, and in the year 1870 the writer adopted the plan of placing the samples in long glass cylinders which were held in a frame in such manner that the images of the glass bottoms of the cylinders could be viewed side by side in a mirror. This arrangement was found to present marked advantages in the case of a fluorescent liquid like petroleum, but the system was open to the objection that the standard samples were very liable to become altered in colour, and required to be frequently verified and corrected by experts. Moreover, the adoption by the Petroleum Association of London of precise conditions of contract necessitated the provision of a more accurate and unerring test of colour. Accordingly, the Committee of the Petroleum Association decided, under the advice of the writer, to employ an instrument devised by Mr. R. P. Wilson for use with stained glass standards. This apparatus (Fig. 1), which has admirably fulfilled the object in view, consists of two similar tubes, closed at each end by a screw cap carrying a disc of stout glass. These tubes are placed on a stand at a convenient angle above a small mirror, by means of which light is reflected upwards through them. At the upper ends of the tubes is a box containing two pairs of prisms so arranged that the light passing from the mirror

is twice reflected, and is thus brought into an eye-piece surmounting the box. One of the tubes is completely filled with the sample of oil to be tested, the length of the column of liquid being sixteen inches, and beneath the other tube, which remains empty, a disc of stained glass is placed. On applying the eye to the eye-piece the circular field is seen to be divided through the centre by a sharp line formed by the junction of the prisms, the two halves being tinted to an extent corresponding with the colour of the oil and that of the standard glass respectively. The glass standards representing the various grades of colour recognised in the trade are prepared by the Tintometer, Ltd., of Salisbury. They are five in number, and are thus designated :

1. Water white.
2. Superfine white.
3. Prime white.
4. Standard white.
5. Good merchantable.

The Wilson chromometer admits of an accurate comparison being made, but where the colour of the sample lies between those of two standards, there is an absence of precision in the

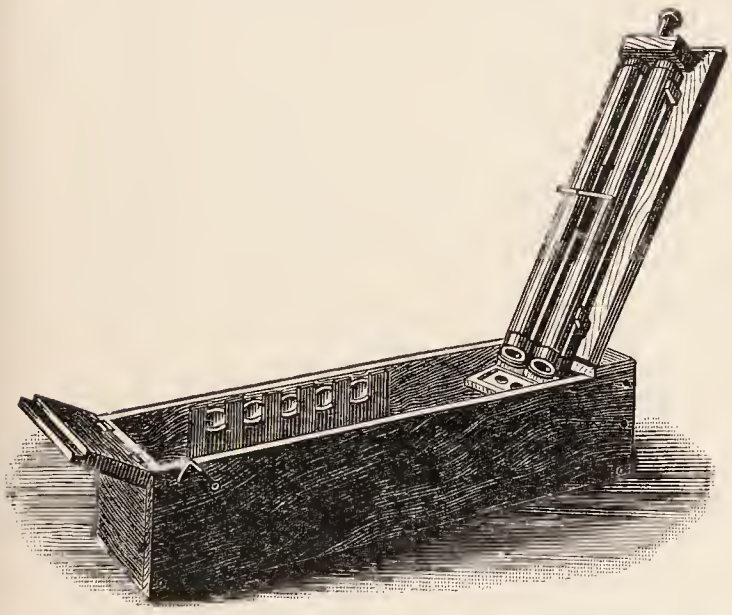


Fig. 1.

statement of the result of the test. This is not attended with any practical inconvenience where the instrument is simply used for ordinary routine work, but the writer has frequently found it necessary to record the precise colour of a sample, or to state by how much that colour falls short of a stipulated grade. To meet this want a modification of the chromometer already described was designed by Stammer. In this apparatus there is a provision for shortening the length of the column of oil, so that, starting with a standard of somewhat paler tint than the oil, the colour of the oil may be registered in terms of the standard. Messrs. Schmidt and Haensch, the well-known philosophical instrument makers of Berlin, have devoted a good deal of attention to the improvement of Stammer's original instrument, and have devised a colorimeter which the writer has used, and of which he has formed a favourable opinion. In the construction of this apparatus (Fig. 2) Messrs. Schmidt and Haensch have desired to provide for the use of only one glass standard, so that all recorded determinations of colour may be strictly comparable. This would be a distinct advantage, since the relation between the various standards enumerated is a purely arbitrary one ; but unfortunately the range of colour is necessarily so wide that if a standard suitable for water-white oil is employed, the column needs to be so much decreased in length for oils of

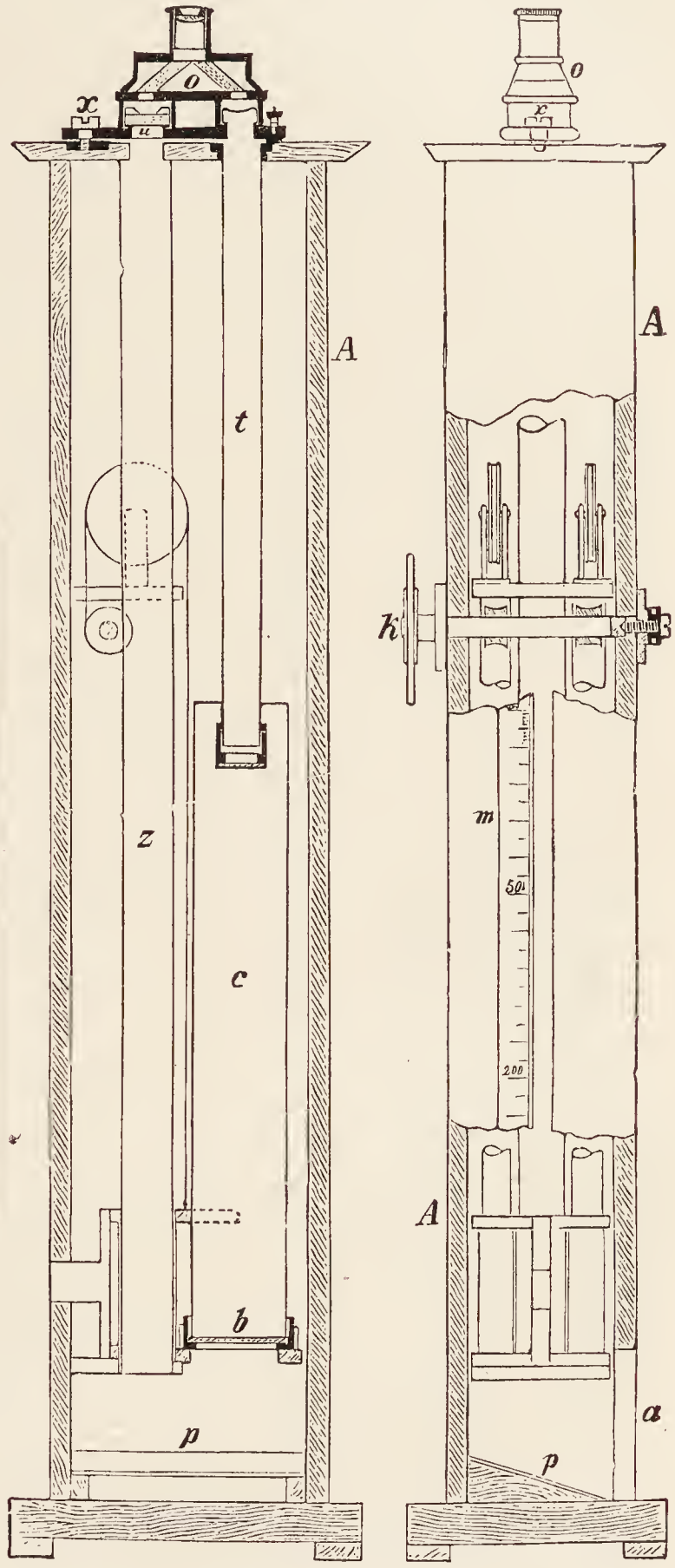


Fig. 2.

A. Case. *a*. Opening for passage of light to reflector. *b*, *c*. Cylinder, with glass bottom, for oil under examination. *k*. Hand-wheel for raising or lowering cylinder *b*, *c*. *m*. Graduated scale showing length of column of oil through which light is passing. *o*. Optical arrangement (prisms and eye-piece). *p*. Reflector to project light upwards through the parallel tubes and the prisms into the eye-piece. *t*. Tube closed at the bottom by a glass plate. *u*. Coloured glass disc. *x*. Screw on which the optical arrangement may be turned to insert or remove the disc *u*. *z*. Tube, open at both ends.

comparatively dark colour that the sensitiveness of the instrument is seriously impaired. To overcome this defect, Mr. Robert Redwood has made several important alterations in the instrument, which, while largely increasing its

sensitiveness, admit of the colour of any sample of kerosene being precisely recorded on a scale ranging from water white (1) to good merchantable (5), the space between any two of the colours being divided into ten equal parts, so that the colour of a sample midway between water white and superfine white would be expressed as 1·5. This instrument has been in use in the writer's laboratory for many years, and has given very satisfactory results.

(*b*) *Odour.*—The determination of odour requires considerable experience, as it is necessarily a matter of judgment, and due consideration has to be given to the origin and grade of the oil. It is usual to certify that the odour is good merchantable, or not good merchantable, as the case may be.

(*c*) *Specific gravity.*—This is ordinarily determined by the use of a hydrometer, but the Westphal or the Sartorius specific gravity balance will often be found a preferable instrument. In the case of oil imported in bulk, where the weight of the oil is calculated from the volume at a given temperature, the specific gravity should be accurately determined by the use of the specific gravity bottle.

(*d*) *Flashing-point and fire-test.*—This is, at any rate from one point of view, by far the most important test to which kerosene is subjected, since the petroleum trade is in most parts of the world conducted under legal restrictions in regard to the temperature at which the oil either commences to evolve inflammable vapour or takes fire and continues to burn. The manufacturer of kerosene has on the one hand to avoid introducing into or leaving in the oil such of the more volatile hydrocarbons as would either actually or in the opinion of the Legislature render the fluid unsafe for use in lamps of the ordinary construction, and on the other hand to arrest the collection of the kerosene distillate before the process of distillation has resulted in the addition to the product of the denser hydrocarbons in such quantity as to impair the burning quality. The limitation of the specific gravity was found to be an effectual means of preventing the introduction into the oil of an undue proportion of the heavier hydrocarbons, but afforded no check upon the inflammability of the oil; accordingly, in the early days of the petroleum industry, it was customary in the United States to test the oil by pouring it upon warm water and applying a lighted taper to the surface, or by warming the oil in a cup placed in hot water, and applying a flame, the temperature at which the oil gave off ignitable vapour being termed the 'flashing-point,' and that at which it took fire the 'fire-test.' When, however, it became recognised that legal restrictions in regard to the inflammability of kerosene were necessary in the interests of public safety, special forms of apparatus for the testing of flashing-point and igniting-point were devised. The earliest of these testing instruments, known as Tagliabue's open-cup tester (Fig. 3), was constructed by an instrument-maker of that name in New York. It consists simply of a glass cup to hold the oil, placed in a small copper water-bath, heated by a spirit lamp. A thermometer is suspended in the oil, and the temperature is noted at which, on passing a lighted splinter of wood across the surface of the oil, there is either a flash of ignited vapour, or on a further increase of temperature the oil ignites and continues to burn. The English Petroleum Act, passed on July 29, 1862, provided that 'Petroleum for the purposes of this Act shall include any product thereof that gives off an inflammable vapour at less than 100° of Fahrenheit's thermometer.' The method of testing was, however, not defined, and the Act was practically inoperative. Accordingly, on July 13, 1868, an amending Act was passed, which prescribed the form of apparatus and method of testing to be adopted and defined 'petroleum' for the purposes of the two Acts as including 'all such rock oil, Rangoon oil, Burmah oil, any product of them, and any oil made from petroleum, coal, schist, shale, peat, or other bituminous substance, and any product of them, as gives off an inflammable vapour at a temperature of less than 100° of Fahrenheit's thermometer.' The prescribed apparatus for testing consists of a slightly conical oil-cup of thin sheet-iron, provided with a flat rim, and a raised edge $\frac{1}{4}$ in. high. Across the cup and fixed to or resting on the edge is a wire, which is thus $\frac{1}{4}$ in. above the flat rim. The oil-cup is supported by the rim in a tin water-bath. The outer vessel having been filled with 'cold or nearly cold water,' as much of the oil to be tested is poured into the cup as will fill it without flowing over the flat rim, and a thermometer with a round bulb, and so graduated that every 10°F. occupies not less than $\frac{1}{2}$ in. on the scale, is then suspended in the oil so that the bulb is immersed about $1\frac{1}{2}$ in. beneath the surface. A screen of paste-board or wood of specified dimensions having been placed round the apparatus, a 'small' flame is applied to the bottom of the water-bath, and when the temperature of the oil has reached 90°F., a 'very small' flame is passed across the surface of the oil on a level with the wire, this application of the test-flame being repeated for every rise of 'two or three' degrees in temperature, until a 'pale-blue flicker or flash' is produced. The temperature at which this occurs having been noted, the experiment is repeated with a fresh sample of the oil, withdrawing the source of heat when the temperature approaches that noted in the first experiment, and applying the test-flame at every rise of two degrees.

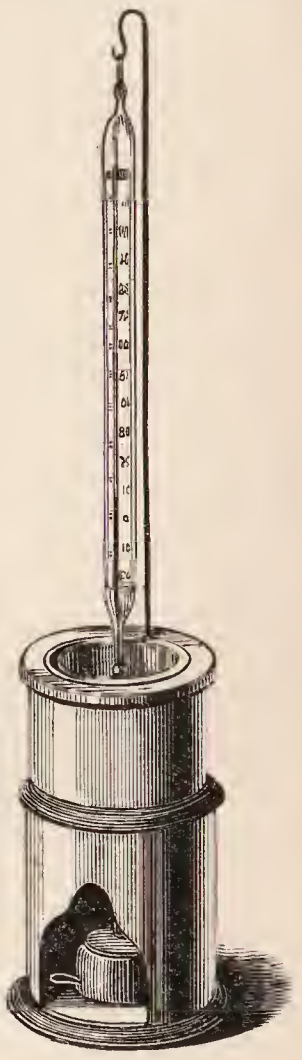


Fig. 3.

The greater part of the earlier petroleum legislation in the United States was based upon fire-test and not upon flashing-point, but in several of the States the petroleum laws now prescribe a test of flashing-point. In 1879 the New York Produce Exchange adopted the Saybolt Electric Tester (Fig. 4), which is an open cup instrument wherein the ignition is effected

by means of an electric spark from a small induction coil, the spark being caused to pass when required between platinum points at a fixed distance above the surface of the oil. The official directions for the use of the apparatus are as follows :—

'Fill the metal bath with water, leaving room for displacement by the glass cup. Heat the water until the bath thermometer indicates 100°F., at which point remove the lamp. Fill the glass cup with oil to top line, indicated by the rim surrounding cup, which is one-eighth of an inch below top edge of the cup. See that there is no oil on the outside of the cup, nor upon the upper level edge, using paper to clean cup in preference to cotton or woollen material. See that the surface of the oil is free from air bubbles before first flash is produced. Lift the cup steadily with left hand and place in the bath. Suspend the thermometer with the bulb of same immersed just from view under the surface of oil. Adjust the flashing bar and immerse the battery zincs in fluid. Try for first flash every degree until the same is obtained.

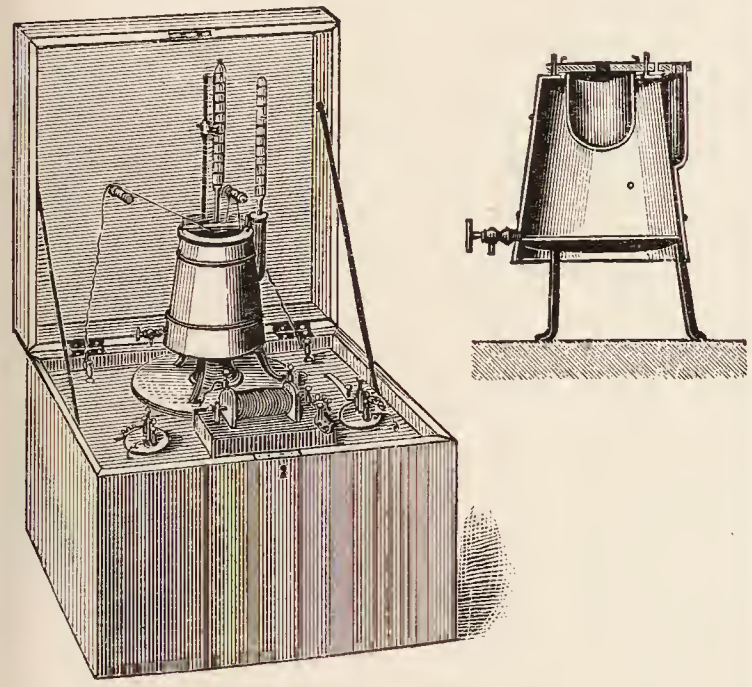


Fig. 4.

Attain flash by producing spark with one stroke of the key. The stroke on the key should be such as in telegraphy is used to produce what is called a dot, that is a short quick stroke. The first flash produced from 110° test oil is generally obtained when the temperature of the oil has arrived at 90°. The temperature of the bath at 100° (as per note above) will carry the oil to about 90°, or, in other words, to about the first flashing-point, without the aid of a lamp. When the thermometer in the oil indicates 90°, introduce lamp under the bath, and do not remove until the operation is finished. The temperature of oil when placed in bath should not be lower than 55° nor higher than 70°F. The flashing bar must be free from oil before adjusting for test. Draughts of air must be excluded from the apartment wherein tests are made. Oil of 110° and upwards shall (after first flash) be flashed at 95, 100, 104, 108, 110, 112, 115. Oil of 120° and upwards, after first flash, 100, 105, 110, 115, 118, 120, 122, 125. Oil of 130° and upwards, every five degrees after first flash, until burning-point.'

Prior to the introduction of the Saybolt Tester, Arnaboldi constructed an open-cup tester similar to Tagliabue's, but of greater capacity, and provided with a mechanical arrangement for passing the test-flame over the oil.

The directions for applying the test given in the English Petroleum Act of 1868 were found to be insufficiently precise, and much difference of opinion existed as to the interpretation of the words 'small flame' and 'very small flame,' with the result that dealers were proceeded against, and in some cases convicted of selling kerosene declared by the local authorities to have a flashing-point below the legal limit of 100°F., but which had been tested by independent experts with satisfactory results. Moreover, the open-cup system of testing was found by experience to be incapable of furnishing trustworthy results in the hands of unskilled persons.

Accordingly, Mr. Keates, in his capacity of consulting chemist of the Metropolitan Board of Works, suggested the substitution of a closed cup (Fig. 5) for the open one, and in 1871 a Bill to legalise this alteration, as well as to amend the law in several other respects, was introduced into Parliament. In consequence, however, of the test standard or limit having been fixed by Mr. Keates at a point (85°) which it was contended was considerably higher than the equivalent of the existing standard, the Bill was opposed by the petroleum trade, and the proposal to change the form of apparatus was withdrawn; the Bill, which passed through the final stage on August 11 in that year, repealing the two previous Acts, but again prescribing the use of the open test specified in the Act of 1868. In the following year the subject of petroleum testing was inquired into by a Select Committee of the House of Lords, and a great deal of conflicting evidence was taken, but no satisfactory conclusion was arrived at. Therefore, in July, 1875, with the concurrence and approval of the Metropolitan Board of Works and of the Petroleum Association, Sir Frederick Abel was requested by the Government to undertake an investigation with the object of placing the subject of petroleum testing upon a satisfactory basis. The formulated questions submitted to Sir Frederick Abel were the following :

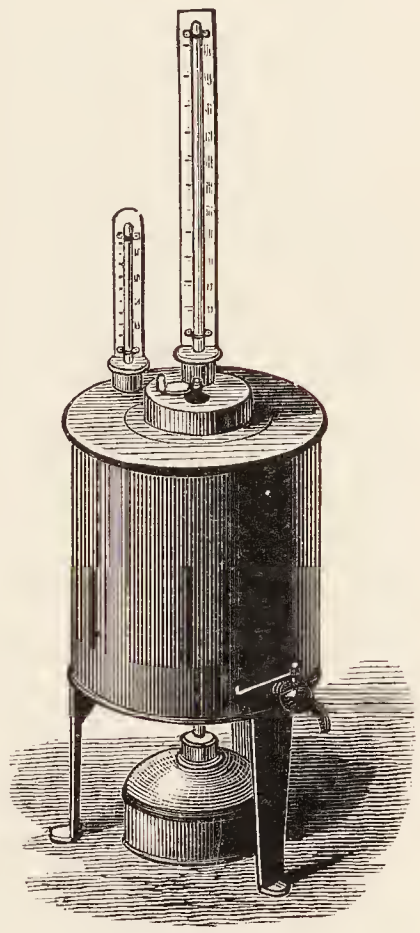


Fig. 5.

'1. Whether the method of testing petroleum as prescribed in Schedule 1 of the Petroleum Act, 1871 (34 & 35 Vict. c. 105), is such as uniformly to ensure reliable and satisfactory results.

'2. If not, what alterations in the method of testing petroleum should be adopted to secure such results, due regard being had to the fact that the testing must, in many instances, be carried out by persons who have had

comparatively little experience in conducting delicate experiments.

'3. Assuming it to be, in your opinion, desirable to obtain a "flashing-test" for petroleum, whether the present "flashing-point" of 100°F. (or its equivalent under any modified method of testing which you may propose) is, in your judgment, calculated to afford adequate protection to the public, without unduly interfering with or restricting the trade; if not, what alteration in this respect should be made.'

After a prolonged and exhaustive experimental inquiry, in which Dr. Kellner rendered valuable assistance, Sir Frederick Abel presented to the Secretary of State an elaborate report, dated August 12, 1876, wherein the questions enumerated were thus answered:

(1) The method of testing petroleum as prescribed in Schedule 1 of the Petroleum Act, 1871 (34 & 35 Vict. c. 105), is not 'of a nature uniformly to ensure reliable and satisfactory results.'

(2) A method of testing petroleum has been elaborated for adoption in place of that prescribed by the Petroleum Act, 1871, due regard having been had to the fact 'that the testing must in many instances be carried out by persons who have had comparatively little experience in conducting delicate experiments.' This method, while resembling in its general nature the one hitherto used, is free from the defects inherent in the latter, and is so arranged that it can be carried out, with the certainty of furnishing uniform and precise results, by persons possessing no special knowledge or skill in manipulation. With ordinary attention in the first instance to simple instructions, different operators cannot fail to obtain concordant results with it, and it is so nearly automatic in its nature that it is not, like the present method of testing, susceptible of manipulation so as to furnish different results at the will of the operator.

(3) There are not, in my judgment, any well-established grounds for considering that the present flashing-point of 100°F. is not 'calculated to afford adequate protection to the public.'

(4) With the employment of the new test, a minimum flashing-point should therefore be adopted, which is equivalent, or as nearly as possible so, to the flashing-point of 100°F., as furnished by the present test.

It will be obvious that the determination of the equivalent test standard was not an easy part of Sir Frederick Abel's task, since the Abel tester furnishes no exception to the rule that the flashing-point of a given example of petroleum is far lower in a closed than in an open vessel, and it was therefore necessary to deal with the conflicting views already referred to as to the proper mode of conducting the test with the open-cup instrument in order to determine the equivalent standard. The writer assisted Sir Frederick Abel in the conduct of this portion of the inquiry, but before the test standard was even provisionally fixed, Mr. T. W. Keates, as representing the Metropolitan Board of Works, and Mr. John Calderwood, on behalf of the Scottish Mineral Oil Association, were also consulted. Eventually, as the result of the joint experiments, it was decided that the difference between the flashing-points obtained with the open-cup instrument and the Abel tester ranged from 25° to 29°F. Adopting the mean difference of 27°, the new standard was accordingly fixed at 73°F.

After the presentation of the report, the writer proceeded to apply the two tests to 1,000 representative samples of kerosene, with the result that the figures provisionally adopted were confirmed.

The ultimate outcome of Sir Frederick Abel's painstaking investigation was the legislation by Parliament, on August 11, 1879, of what is now so well known as the Abel Test. The instrument and its use are thus described in the Petroleum Act:—

First Schedule.—Mode of testing petroleum so as to ascertain the temperature at which it will give off inflammable vapour.

Specification of the test apparatus

(Figs. 6, 7, and 8).

The following is a description of the details of the apparatus:—

The oil cup (Fig. 6) consists of a cylindrical vessel 2″ diameter, $2\frac{2}{10}$″ height (internal), with outward projecting rim $\frac{5}{10}$″ wide, $\frac{3}{8}$″ from the top, and $1\frac{7}{8}$″ from the bottom of the cup. It is made of gun-metal or brass (17 B.W.G.) tinned inside. A bracket, consisting of a short stout piece of wire bent upwards and terminating in a point, is fixed to the inside of the cup to serve as a gauge. The distance of the point from the bottom of the cup is $1\frac{1}{2}$″. The cup is provided with a close-fitting overlapping cover made of brass (22 B.W.G.), which carries the thermometer and test lamp. The latter is suspended from two supports from the side by means of trunnions, upon which it may be made to oscillate; it is provided with a spout, the mouth of which is one-sixteenth of an inch in diameter. The socket which is to hold the thermometer is fixed at such an angle and its length is so adjusted that the bulb of the thermometer, when inserted to its full depth, shall be $1\frac{1}{2}$″ below the centre of the lid.

The cover is provided with three square holes—one in the centre, $\frac{5}{10}$″ by $\frac{4}{10}$″, and two smaller ones, $\frac{3}{10}$″ by $\frac{2}{10}$″, close to the sides and opposite each other. These three holes may be closed and uncovered by means of a slide moving in grooves, and having perforations corresponding to those on the lid.

In moving the slide so as to uncover the holes, the oscillating lamp is caught by a pin fixed in the slide, and tilted in such a way as to bring the end of the spout just below the surface of the lid (Fig. 7). Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position.

Upon the cover, in front of and in line with the mouth of the lamp, is fixed a white bead, the dimensions of which represent the size of the test-flame to be used.

The bath or heating vessel (Fig. 8) consists of two flat-bottomed copper cylinders (24 B.W.G.) —an inner one of 3″ diameter and $2\frac{1}{2}$″ height, and an outer one of $5\frac{1}{2}$″ diameter and $5\frac{3}{4}$″ height; they are soldered to a circular copper plate (20 B.W.G.) perforated in the centre, which forms the top of the bath, in such a manner as to

inclose the space between the two cylinders, but leaving access to the inner cylinder. The top of the bath projects both outwards and inwards about $\frac{3}{8}''$; that is, its diameter is about $\frac{5}{8}''$ greater than the body of the bath, while the diameter of the circular opening in the centre is about the same amount less than that of the inner copper cylinder. To the inner projection of the top is fastened, by six small screws, a flat ring of ebonite, the screws being sunk below the surface of the ebonite to avoid metallic contact between the bath and the oil cup. The exact distance between the sides and bottom of the bath and of the oil cup is one-half of an inch. A split socket similar to that on the cover of the oil cup, but set at a right angle, allows a thermometer to be inserted into the space between the two cylinders. The bath is further provided with a funnel, an overflow pipe, and two loop handles.

The bath rests upon a cast-iron tripod stand, to the ring of which is attached a copper cylinder or jacket (24 B.W.G.) flanged at the top, and of such dimensions that the bath, while firmly resting on the iron ring, just touches with its projecting top the inward-turned flange. The diameter of this outer jacket is $6\frac{1}{2}''$. One of the three legs of the stand serves as a support for

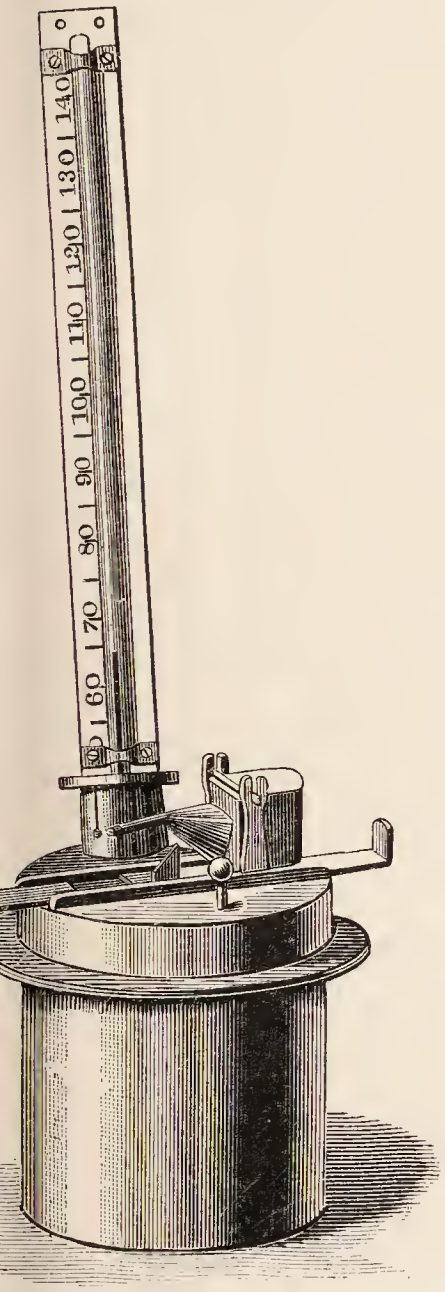


Fig. 6.

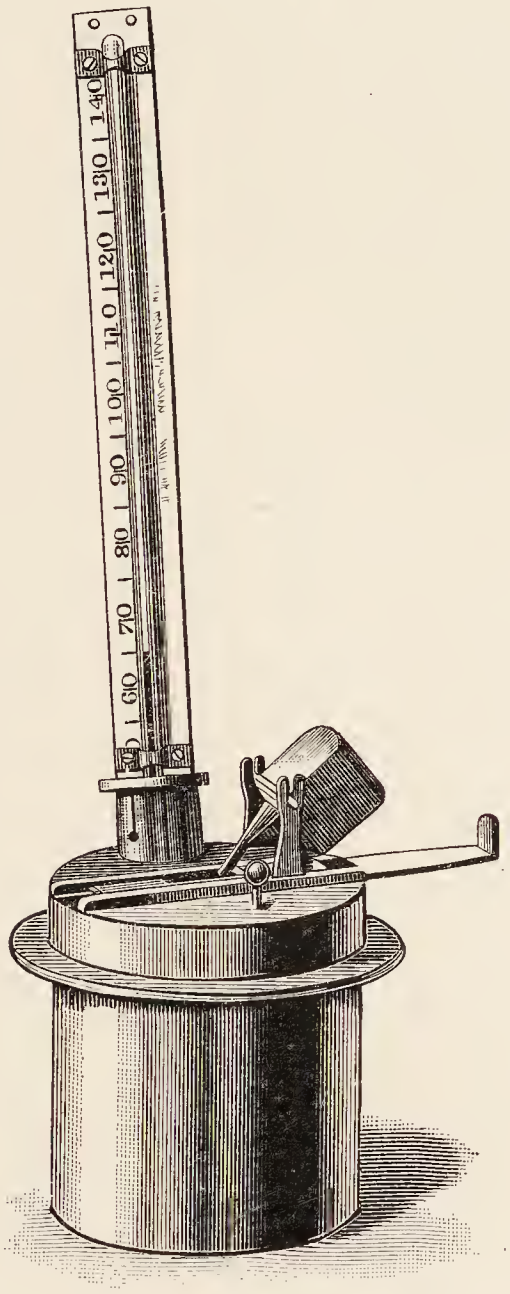


Fig. 7.

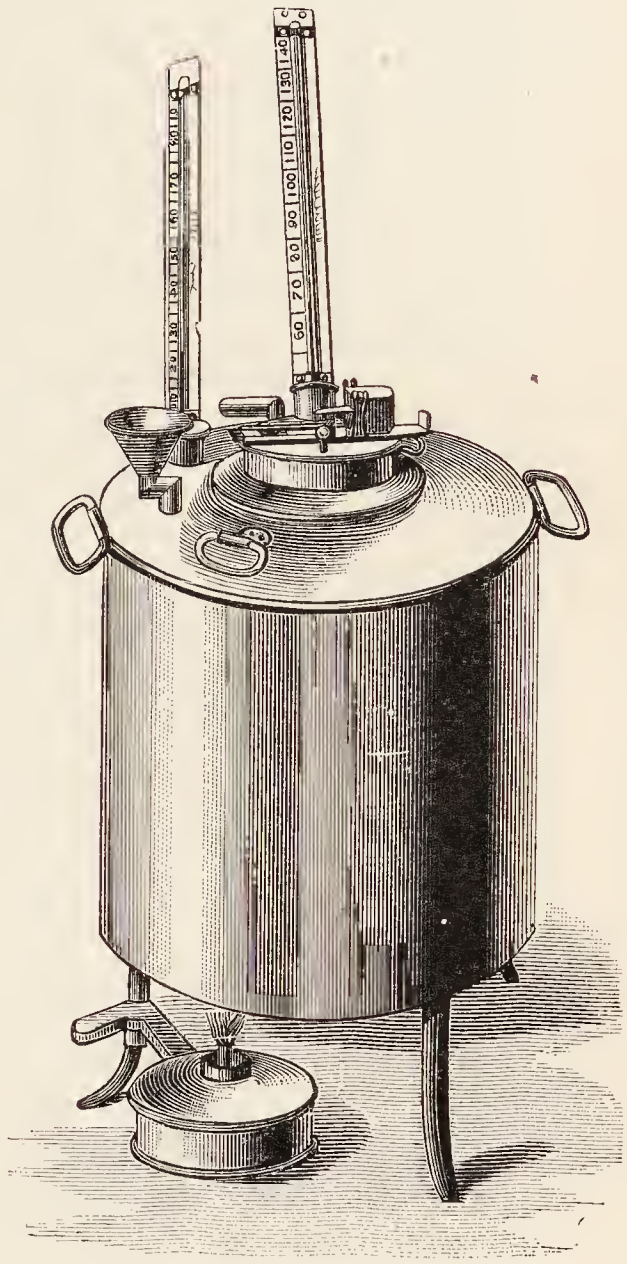


Fig. 8.

the spirit lamp attached to it by means of a small swing bracket. The distance of the wick holder from the bottom of the bath is $1''$.

Two thermometers are provided with the apparatus—the one for ascertaining the temperature of the bath, the other for determining the flashing-point. The thermometer for ascertaining the temperature of the water has a long bulb and a space at the top. Its range is from about 90° to 190° Fahrenheit. The scale (in degrees of Fahrenheit) is marked on an ivory back fastened to the tube in the usual way. It is fitted with a metal collar, fitting the socket, and the part of the tube below the scale should have a length of about $3\frac{1}{2}''$, measured from the lower end of the scale to the end of the bulb. The thermometer for ascertaining the temperature of the oil is fitted with collar and ivory scale in a similar manner to the one described. It has a round bulb, a space at the top, and ranges from about 55°F. to 150°F.; it measures from end of ivory back to bulb $2\frac{1}{4}''$.

Note.—A model apparatus is deposited at the Weights and Measures Department of the Board of Trade.

Directions for applying the flashing-test.

1. The test apparatus is to be placed for use in a position where it is not exposed to currents of air or draughts.

2. The heating vessel or water-bath is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel. The temperature of the water at the commencement of the test is to be 130°F., and this is attained

in the first instance either by mixing hot and cold water in the bath, or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or by heating the water with the spirit lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

If the water has been heated too highly, it is easily reduced to 130° by pouring in cold water little by little (to replace a portion of the warm water) until the thermometer gives the proper reading.

When a test has been completed, this water-bath is again raised to 130° by placing the lamp underneath, and the result is readily obtained while the petroleum cup is being emptied, cooled, and refilled with a fresh sample to be tested. The lamp is then turned on its swivel from under the apparatus, and the next test is proceeded with.

3. The test lamp is prepared for use by fitting it with a piece of flat plaited candle-wick, and filling it with colza or rape oil up to the lower edge of the opening of the spout or wick tube. The lamp is trimmed so that when lighted it gives a flame of about 0·15 of an inch diameter, and this size of flame, which is represented by the projecting white bead on the cover of the oil cup, is readily maintained by simple manipulation from time to time with a small wire trimmer.

When gas is available it may be conveniently used in place of the little oil-lamp, and for this purpose a test-flame arrangement for use with gas may be substituted for the lamp.

4. The bath having been raised to the proper temperature, the oil to be tested is introduced into the petroleum cup, being poured in slowly until the level of the liquid just reaches the point of the gauge which is fixed in the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be observed in the first instance, and if it exceeds 65° the samples to be tested should be cooled down (to about 60°) by immersing the bottles containing them in cold water, or by any other convenient method. The lid of the cup, with the slide closed, is then put on, and the cup is placed into the bath or heating vessel. The thermometer in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position is not under any circumstances to be altered. When the cup has been placed in the proper position, the scale of the thermometer faces the operator.

5. The test-lamp is then placed in position upon the lid of the cup, the lead-line or pendulum,[1] which has been fixed in a convenient position in front of the operator, is set in motion, and the rise of the thermometer in the petroleum cup is watched. When the temperature has reached about 66° the operation of testing is to be commenced, the test flame being applied once for every rise of one degree in the following manner :—

The slide is slowly drawn open while the pendulum performs three oscillations, and is closed during the fourth oscillation.

[1] The pendulum is 24 inches in length from the point of suspension to the centre of gravity of the weight. The writer has found it convenient to employ a synchronised metronome.

Note.—If it is desired to employ the test apparatus to determine the flashing-point of oils of very low volatility, the mode of proceeding is to be modified as follows :—

The air-chamber which surrounds the cup is filled with cold water to a depth of 1½ inches, and the heating-vessel or water-bath is filled as usual, but also with cold water. The lamp is then placed under the apparatus, and kept there during the entire operation. If a very heavy oil is being dealt with, the operation may be commenced with water previously heated to 120°F. instead of with cold water.[1]

In order to deal with the difficulty arising from the sluggish flow of the convection currents, and the consequent low reading of the thermometer, when viscous samples are tested, and, in addition, to make provision for the testing of solid petroleum mixtures, an Order in Council (Statutory Rules and Orders, 1907, No. 483) was issued on May 7, 1907, the Schedule of which is as follows :—

Schedule.—Directions for Testing Petroleum Mixtures.

1. *Liquid Mixtures.* Where the petroleum mixture is wholly liquid, flows quite freely, and does not contain any sediment or thickening ingredient, such mixture shall be tested in the manner set forth in Schedule One to the Petroleum Act, 1879.

2. *Viscous and Sedimentary Mixtures.* Where the petroleum mixture contains an undissolved sediment, as in the case of some metal polishes, which can be separated by filtration or by settlement and decantation, the sediment may be so separated and the decanted liquid may be tested in the manner set forth in Schedule One to the Petroleum Act, 1879.

In carrying out such separation, care must be taken to minimise the evaporation of the petroleum. The separation of the sediment must not be effected by distillation.

Where the petroleum mixture is such that sediment cannot be separated by the aforementioned means, or where it is of a viscous nature, as in the case of indiarubber solution, quick-drying paints, &c., such mixture shall be tested in the apparatus modified as shown in the drawing hereto. This apparatus differs from that prescribed in Schedule One to the Petroleum Act, 1879, only in the addition of a stirrer to equalise the temperature throughout the sample under test.

In carrying out the test of a viscous petroleum mixture, this stirrer shall be constantly revolved at a slow speed with the fingers, except when applying the test flame, the direction of revolution being that of the hand of a clock.

With the exception of the use of the stirrer, the manner of carrying out the test shall be that set forth in Schedule One to the Petroleum Act, 1879.

The stirrer may be removed by grasping the spindle just above the blades with the finger and thumb, and unscrewing the upper sheath. The opening in the lid, through which the stirrer

[1] A preferable method is to keep the temperature of the water-bath at 130°F. and place water to a depth of a quarter of an inch in the air space.

passes, may then be closed by a plug provided for the purpose.

When this has been done, the apparatus shall be deemed to comply with the specification set forth in Schedule One of the Petroleum Act, 1879, and may be used for testing ordinary petroleum or solid petroleum mixtures.

A model of the afore-mentioned apparatus will be deposited with the Board of Trade, and the provisions of section 3 of the Petroleum Act, 1879, in regard to verification and stamping shall apply also to such apparatus as though it were the apparatus prescribed by the said Act.

For the purpose of carrying out such verification the stirrer shall be removed and the opening plugged as hereinbefore directed. The apparatus shall then be tested with ordinary petroleum. The stirrer shall be verified by comparison of measurements.

3. *Solid petroleum mixtures.* Where the petroleum mixture is solid, as in the case of naphtha soaps, &c., the apparatus to be used for the test shall be that prescribed in Schedule One of the Petroleum Act, 1879.

The method of carrying out the test of such solid mixture shall be as follows :—

The solid mixture must be cut into cylinders $1\frac{1}{2}$ inches long and $\frac{1}{4}$ inch in diameter by means of a cork borer or other cylindrical cutter having the correct internal diameter. These cylinders are to be placed in the petroleum cup of the testing apparatus in a vertical position in such number as will completely fill the cup. The cylinders must be in contact with one another, but must not be so tightly packed as to be deformed in shape.

Five or six of the cylinders in the centre of the cup must be shortened to $\frac{1}{2}$ inch to allow space for the thermometer bulb.

The air bath of the testing apparatus must be filled to a depth of $1\frac{1}{2}$ inches with water. The water-bath must then be raised to and maintained at a temperature of about 75°F.

The cup must then be placed in the air bath, and the temperature of the sample must be allowed to rise until the thermometer in the oil cup shows 72°F., when the test flame must be applied.

If no flash is obtained, this temperature must be maintained constant in the oil-cup for 1 hour, at the expiration of which time the test flame must again be applied.

If a flash is obtained, the solid mixture will be subject to the provisions of the Petroleum Acts in virtue of this Order.

Note.—It may in many cases save time in testing samples of petroleum mixtures to apply the test flame after the sample has been a few minutes in the cup and while still at the temperature of the room in which the test is being carried out, provided that this temperature is below 73°F. If a flash is obtained by this means, it is unnecessary to proceed with the test at a higher temperature.

In 1880 the subject of petroleum-testing was investigated in Germany by the direction of the Government, and a considerable number of experiments were made with different forms of apparatus. Eventually the Abel instrument was selected as the best, but exception was taken to the personal error liable to be introduced by the method of applying the test-flame, and accordingly a clockwork arrangement for moving the test-slide and bringing the igniting flame to the required position was added (Fig. 9). The clockwork movement, which is fixed to the cover of the oil cup, is wound up prior to each application of the test-flame, and is released by pressing a trigger as the mercury in the thermometer reaches each $\frac{1}{2}$°C. The mechanism is so adjusted that the rate of opening and closing the test-orifice is properly timed, and the operator is therefore relieved from the necessity of timing the movement by the aid of a pendulum. The English Abel apparatus is provided with both oil-lamp and gas arrangement for igniting the vapour, but the German instrument has the oil-lamp only, as it was found that the two appliances did not give in all cases concordant results, and petroleum has advantageously been substituted for colza oil for use in the test-lamp.

Before the Abel tester had been very long in use it was found that the results afforded were materially affected by the amount of atmospheric pressure. This source of variation in flashing-point had not previously received attention, and was first accidentally observed in Germany. As the result of a series of experiments conducted in an air-tight chamber in the Jewish Hospital in Berlin at different atmospheric pressures, it was found that the difference in flashing-point amounted to about 0·30°C. for 10 mm. in the height of the barometric column, and accordingly a table of corrections was framed on this basis for use with the Abel tester in Germany. With the object of procuring some tangible evidence of the effect of barometric changes upon the flashing-point, the writer conducted, in association with Sir Frederick Abel, a series of tests at different altitudes in Switzerland, and obtained corroborative results, the observed variations in flashing-point being at the rate of 2°F. for 1 inch of barometric pressure. These experiments were, however, not made with a view of determining with precision the extent of variation, the number of tests made in the limited time being too few to justify the basing of a table of corrections on the results.

At a later date an additional source of discrepancies in the results afforded by the Abel instrument was discovered in the effect of a tropical temperature upon the liberation of vapour from the oil. The Indian Government, having adopted the Abel apparatus, had copied verbatim from the English Act the directions for applying the test, and attention was forcibly directed to the source of variations alluded to by the condemnation of several cargoes of kerosene, which had arrived in the port of Calcutta. The writer proceeded to India to investigate the matter, and as the result of experiments made in that country and of a series of tests conducted by Sir Frederick Abel and the writer, with the assistance of Dr. Kellner, in an apartment at Woolwich Arsenal heated to a tropical temperature, it was found that a much lower flashing-point than that furnished in a temperate climate was liable to be obtained when the Abel test was applied in a tropical country in the manner prescribed by the English Act. Further experiments made by Dr. Warden, analyst to the Government of Bengal, Professor Pedler of Calcutta, Dr. Lyon, Sir Frederick Abel, Dr. Kellner,

and the writer, showed that the apparent depression of the flashing point was largely due to the vapour which became disengaged in the act of filling the oil-cup. Prolonged cooling of the oil appeared to reduce the liability of this disengagement of vapour, but the only practically available method of eliminating this source of discrepancies was found to be the adoption of some expedient for getting rid of the vapour before commencing the operation of testing or before the flashing-point of the oil was reached. Various methods of effecting this object were tried. The vapour was easily removed by gently blowing over the surface of the oil before placing the cover on the cup, or by the use of an aspirator attached to the cover, or by leaving the test-slide withdrawn for some time; but it was ultimately decided to recommend the commencement of the test many degrees below the flashing-point, so that the disengaged vapour might be removed by the current of air created by the test-flame in successive quantities too small to cause a flash before the active volatilisation of the oil began. With this modification in

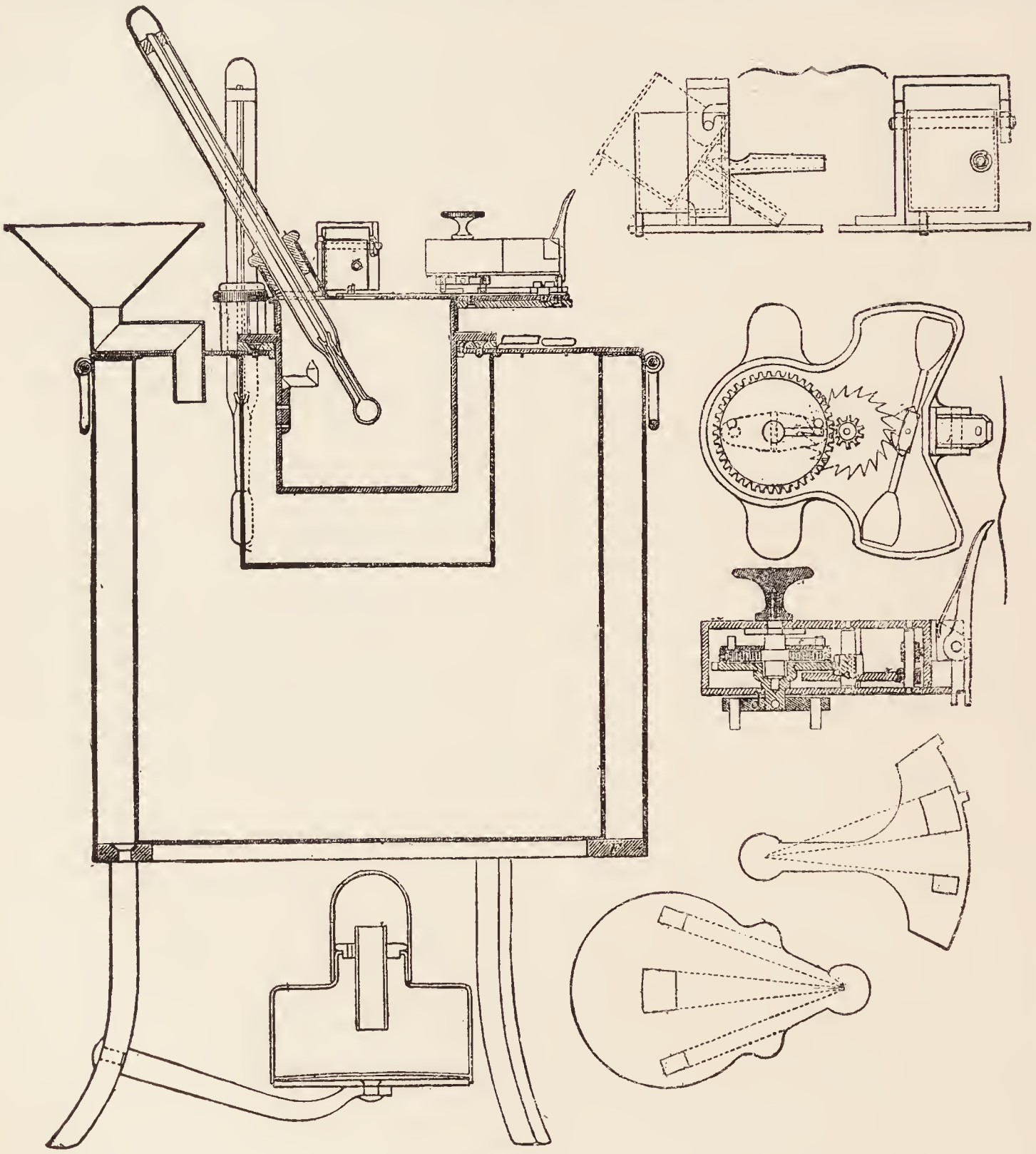


Fig. 9.

the method of applying the test in a tropical country, the apparatus is caused to give results which agree very closely with those which it furnishes in a temperate climate. Obviously, a portion of the volatile constituents of the oil becomes dissipated in this mode of conducting the test, but, since kerosene cannot be exposed to the air in the tropics without this loss occurring, the defect is not of practical importance. Further details in regard to this question will be found in a joint communication by Sir Frederick Abel and the writer published in the Chemical News on May 2, 1884. In October, 1887, Sir Frederick Abel drew up the following instructions for the use of the Abel tester in temperate and tropical climates :—

Directions for preparing and using apparatus for testing petroleum oil (these directions apply to the use of the Abel tester in temperate climates) :—

1. *Preparing the water-bath.*—The water-bath is filled by pouring water into the funnel until it begins to flow out at the overflow pipe. The temperature of the water at the commencement

of each test, as indicated by the long-bulb thermometer, is to be 130°F., and this is attained in the first instance by mixing hot and cold water, either in the bath or in the vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication, or the water is heated by a spirit lamp (which is attached to the stand of the apparatus) until the required temperature is reached.

2. *Preparing the test-lamp.*—The test-lamp is fitted with a piece of cylindrical wick of such thickness that it fills the wick-holder, but may readily be moved to and fro for the purpose of adjusting the size of the flame. In the body of the lamp, upon the wick, which is coiled within it, is placed a small tuft of cotton-wool moistened with petroleum, any oil not absorbed by the wool being removed. When the lamp has been lighted the flame is adjusted until it is the size of the bead fixed on the cover of the oil-cup.

3. *Filling the oil-cup.*—The oil-cup is placed on a level surface in a good light, and the oil to be tested is poured in without splashing, until its surface is level with the point of the gauge which is fixed in the cup. The oil should be poured from a suitable small vessel, never direct from a large can. The round-bulb thermometer is inserted into the lid of the cup, care being taken that the projecting rim of the collar touches the edge of the socket; the test-lamp, prepared as already described, is placed in position, and the cover put on to the cup and pressed down so that its edge rests on the rim of the cup.

4. *The application of the test.*—The water-bath, with its thermometer in position, is placed in some locality where it is not exposed to currents of air, and where the light is sufficiently subdued to admit of the size of the test-flame being compared with that of the bead on the cover. The cup is carefully lifted without being shaken, placed in the bath, and the test-lamp lighted. The thermometer in the oil-cup is now watched, and when the temperature has reached 66°F. (the sample, if necessary, having previously been cooled to below that temperature by immersing the vessel containing it in cold water), the operation of testing is to be commenced, the test-flame being applied once for every rise of one degree.

If the oil-cup is provided with the automatic (Pensky's) arrangement for opening and shutting the slide, the clockwork is wound up by turning the knob from left to right, and set in motion by pressing the trigger.

If the slide is intended to be moved by hand, it should be drawn open slowly and shut quickly. The exact time to be observed in this operation is regulated by the swing of the pendulum supplied with this form of instrument. The opening of the slide should take the time of three oscillations, the shutting of the slide the time of the fourth oscillation of the pendulum. (By one oscillation is meant the passage of the ball of the pendulum from the greatest distance from the vertical on the one side, to the greatest distance on the other.)

If a flash occurs at the first application of the test-flame (at 66°F.), or at any point below 73°F., the operation is to be repeated with a fresh portion of the oil, which is cooled down to 55°F. before being placed in the cup. The first application of the test-flame is made when the temperature of the oil has reached 60°F.

In repeating a test, a fresh sample of oil must always be used, the tested sample being thrown away.

5. *Correction for atmospheric pressure.*—As the flashing-point of an oil is influenced by changes in atmospheric pressure to an average extent of 1·6°F. for every inch of the barometer, a correction of the observed flashing-point may become necessary. The height of the barometer must, therefore, be determined at the time of making the test for the flashing-point. An aneroid barometer is supplied for this purpose. To facilitate the correction of a flashing-point for pressure a table is appended (see table following the directions for applying the test in hot climates), giving the flashing-points of oils ranging from 65° to 80°F., under pressures ranging from 27 to 31 inches of mercury.

The table is used in the following manner :—

Example.—An oil has given a flashing-point of 71°, the barometer being 28·6; take the nearest number to 71° in the vertical column headed 28·6. This number is 70·8. Substitute for this the number in the same horizontal line in the column headed 30 (the normal height of barometer). The substituted number, *i.e.* the true flashing-point of the oil, is 73°.

The following directions apply to the use of the Abel Petroleum Tester in hot climates :—

Directions for drawing the sample and preparing it for testing.

1. *Drawing the sample.*—In all cases the testing officer, or some person duly authorised by him, shall personally superintend the drawing of the sample from an original unopened tin or other vessel.

An opening sufficiently large to admit of the oil being rapidly poured or siphoned from the tin or other vessel shall be made.

Two bottles, each of the capacity of about forty fluid ounces, are to be filled with the oil. One of these, the contents of which is intended to be preserved for reference in case of need, is to be carefully corked, the cork being well driven home, cut off level with the neck, and melted sealing-wax worked into it. The other bottle may be either stoppered or corked.

2. *Preparing the sample for testing.*—About ten fluid ounces of the oil, sufficient for three tests, are transferred from the bottle into which the sample has been drawn to a pint flask or bottle, which is to be immersed in water artificially cooled until a thermometer, introduced into the oil, indicates a temperature not exceeding 50°F.

Directions for preparing and using the test apparatus.

3. *Preparing the water-bath.*—The water-bath is filled by pouring water into the funnel until it begins to flow out at the overflow-pipe. The temperature of the water at the commencement of each test, as indicated by the long bulb thermometer, is to be 130°F., and this is attained in the first instance by mixing hot and cold water, either in the bath or in a vessel from

which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or the water is heated by means of a spirit-lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

4. *Preparing the test-lamp.*—The test-lamp is fitted with a piece of cylindrical wick of such thickness that it fills the wick-holder, but may readily be moved to and fro for the purpose of adjusting the size of the flame. In the body of the lamp, upon the wick, which is coiled within it, is placed a small tuft of cotton wool, moistened with petroleum, any oil not absorbed by the wool being removed. When the lamp has been lighted, the wick is adjusted by means of a pair of forceps, or a pin, until the flame is the size of the bead fixed on the cover of the oil-cup; should a particular test occupy so long a time that the flame begins to get smaller, through the supply of oil in the lamp becoming exhausted, three or four drops of petroleum are allowed to fall upon the tuft of wool in the lamp from the dropping bottle or pipette provided for the purpose. This can be safely done without interrupting the test.

5. *Filling the oil-cup.*—Before the oil-cup is filled, the lid is to be made ready for being placed upon the cup, *i.e.* the round-bulb thermometer is to be inserted into the socket (so that the projecting rim of the collar with which it is fitted touches the edge of the socket), and the test-lamp is to be placed in position. The oil-cup, having been previously cooled by placing it bottom downwards in water at a temperature not exceeding 50°F., is now to be rapidly wiped dry, placed on a level surface in a good light, and the oil to be tested is poured in without splashing until its surface is level with the point of the gauge which is fitted in the cup. The lid is then put on the cup at once, and pressed down so that its edge rests on the rim of the cup.

6. *Application of the test.*—The water-bath, with its thermometer in position, is placed in some locality where it is not exposed to currents of air, and where the light is sufficiently subdued to admit of the size of the entire test-flame being compared with that of the bead on the cover. The cup is carefully lifted, without shaking it, and placed in the bath, the test-lamp is lighted, and the clockwork wound up by turning the key. The thermometer in the oil-cup is now watched, and when the temperature has reached 56°F. the clockwork is set in motion by pressing the trigger.

If no flash takes place, the clockwork is at once re-wound, and the trigger pressed at 57°F. and so on, at every degree rise of temperature, until the flash occurs, or until a temperature of 95°F. has been reached.

If the flash takes place at any temperature below 77°F. the temperature at which it occurs is to be recorded. The fresh portions of the sample are then to be successively tested in a similar manner and the results recorded. If no greater difference than 2°F. exists between any two of the three recorded results, each result is to be corrected for atmospheric pressure, as hereafter described, and the average of the three corrected results is the flashing-point of the sample. In the event of there being a greater difference than 2°F. between any two of the results, the series of tests is to be rejected, and a fresh series of three similarly obtained, and so on until a sufficiently concordant series is furnished, when the results are to be corrected and the average taken in the manner already described.

No flash which takes place within eight degrees of the temperature at which the testing is commenced shall be accepted as the true flashing-point of the sample tested. In the event of a flash occurring at or below 64° when the test is applied in the manner above described the next testing shall be commenced ten degrees lower than the temperature at which the flash had been previously obtained—that is to say, at 54° or thereunder, and this procedure shall be continued until the results of three consecutive tests do not show a greater difference than 2°.

If a temperature of 76°F. has been reached without a flash occurring, the application of the test-flame is to be continued until a temperature of 95°F. has been reached. If no flash has occurred up to this point, and if the petroleum is declared to be imported subject to the provisions of the Act,[1] the tests shall not be continued, and the testing officer shall certify that the petroleum has a flashing-point of over 95° and is not dangerous. But if the petroleum is oil ordinarily used for lubricating purposes, and is declared to have its flashing-point at or above 200°, or is oil to which a notification of the Governor in Executive Council exempting it from the operation of the Act will be applicable in the event of the flashing-point being found to be at or above 120°, the test shall be continued as follows:—The oil-cup is to be removed from the water-bath, and the temperature of the water in the water-bath is to be reduced to 95°F. by pouring cold water into the funnel (the hot water escaping by the overflow pipe). The air-chamber is then to be filled to a depth of 1½ inches with water at a temperature of about 95°F., the oil-cup is to be replaced in the water-bath, and the spirit-lamp, attached to the water-bath, is to be lighted and placed underneath. The test-flame is then to be again applied from 96°F., at every degree rise of temperature as indicated by the thermometer in the oil-cup until a flash takes place, or until a temperature of 200°F. or 120°F., as the case may be, has been reached. If during this operation the test-flame appears to diminish in size, the lamp is to be replenished in the manner prescribed (at 4) without interrupting the test.

If a flash occurs at any temperature between 76° and 200°F., the temperature at which it occurs, subject to correction for atmospheric pressure, is the flashing-point of the sample.

In repeating a test a fresh sample of oil must always be used, the tested sample being thrown away, and the cup must be wiped dry from any adhering oil, and cooled, as already described, before receiving the fresh sample.

7. *Correction for atmospheric pressure.*—As the flashing-point of an oil is influenced by changes in atmospheric pressure to an average extent of 1·6°F. for every inch of the barometer, a correction of the observed flashing-point may become necessary. The height of the barometer must, therefore, be determined at the time of

[1] The Indian Petroleum Act is here referred to.

making the test for the flashing-point. An aneroid barometer is supplied for this purpose. To facilitate the correction of a flashing-point for pressure a table is appended, giving flashing-points of oils ranging from 65° to 80°F., under pressures ranging from 27 to 31 inches of mercury.

The table is used in the following manner :—

TABLE FOR CORRECTION OF FLASHING-POINTS INDICATED BY THE TEST, FOR VARIATIONS IN BAROMETRIC PRESSURE ON EITHER SIDE OF THIRTY INCHES.

Barometer in Inches.																				
27·0	27·2	27·4	27·6	27·8	28·0	28·2	28·4	28·6	28·8	29·0	29·2	29·4	29·6	29·8	30	30·2	30·4	30·6	30·8	31·0
Flashing-Point in Degrees Fahrenheit.																				
60·2	60·5	60·8	61·2	61·5	61·8	62·1	62·4	62·8	63·1	63·4	63·7	64·0	64·4	64·7	65	65·3	65·6	66·0	66·3	66·6
61·2	61·5	61·8	62·2	62·5	62·8	63·1	63·4	63·8	64·1	64·4	64·7	65·0	65·4	65·7	66	66·3	66·6	67·0	67·3	67·6
62·2	62·5	62·8	63·2	63·5	63·8	64·1	64·4	64·8	65·1	65·4	65·7	66·0	66·4	66·7	67	67·3	67·6	68·0	68·3	68·6
63·2	63·5	63·8	64·2	64·5	64·8	65·1	65·4	65·8	66·1	66·4	66·7	67·0	67·4	67·7	68	68·3	68·6	69·0	69·3	69·6
64·2	64·5	64·8	65·2	65·5	65·8	66·1	66·4	66·8	67·1	67·4	67·7	68·0	68·4	68·7	69	69·3	69·6	70·0	70·3	70·6
65·2	65·5	65·8	66·2	66·5	66·8	67·1	67·4	67·8	68·1	68·4	68·7	69·0	69·4	69·7	70	70·3	70·6	71·0	71·3	71·6
66·2	66·5	66·8	67·2	67·5	67·8	68·1	68·4	68·8	69·1	69·4	69·7	70·0	70·4	70·7	71	71·3	71·6	72·0	72·3	72·6
67·2	67·5	67·8	68·2	68·5	68·8	69·1	69·4	69·8	70·1	70·4	70·7	71·0	71·4	71·7	72	72·3	72·6	73·0	73·3	73·6
68·2	68·5	68·8	69·2	69·5	69·8	70·1	70·4	70·8	71·1	71·4	71·7	72·0	72·4	72·7	73	73·3	73·6	74·0	74·3	74·6
69·2	69·5	69·8	70·2	70·5	70·8	71·1	71·4	71·8	72·1	72·4	72·7	73·0	73·4	73·7	74	74·3	74·6	75·0	75·3	75·6
70·2	70·5	70·8	71·2	71·5	71·8	72·1	72·4	72·8	73·1	73·4	73·7	74·0	74·4	74·7	75	75·3	75·6	76·0	76·3	76·6
71·2	71·5	71·8	72·2	72·5	72·8	73·1	73·4	73·8	74·1	74·4	74·7	75·0	75·4	75·7	76	76·3	76·6	77·0	77·3	77·6
72·2	72·5	72·8	73·2	73·5	73·8	74·1	74·4	74·8	75·1	75·4	75·7	76·0	76·4	76·7	77	77·3	77·6	78.0	78·3	78·6
73·2	73·5	73·8	74·2	74·5	74·8	75·1	75·4	75·8	76·1	76·4	76·7	77·0	77·4	77·7	78	78·3	78·6	79·0	79·3	79·6
74·2	74·5	74·8	75·2	75·5	75·8	76·1	76·4	76·8	77·1	77·4	77·7	78·0	78·4	78·7	79	79·3	79·6	80·0	80·3	80·6
75·2	75·5	75·8	76·2	76·5	76·8	77·1	77·4	77·8	78·1	78·4	78·7	79·0	79·4	79·7	80	80·3	80·6	81·0	81·3	81·6

Example.—An oil has given a flashing-point of 71°, the barometer being at 28·6 ; take the nearest number to 71° in the vertical column headed 28·6. This number is 70·8. Substitute for this the number in the same horizontal line in the column headed 30 (the normal height of the barometer). The substituted number, *i.e.* the true flashing-point of the oil, is 73°.

'Dangerous petroleum' is defined by the Indian Petroleum Act as 'petroleum having its flashing-point below 76° of Fahrenheit's thermometer. Provided that, when all or any of the petroleum on board a ship, or in possession of a dealer, is declared by the master of the ship or the consignee of the cargo, or by the dealer, as the case may be, to be of one uniform quality, the petroleum shall not be deemed to be dangerous if the samples selected from the petroleum have their flashing-points, on an average, at or about 73° of Fahrenheit's thermometer, and if no one of those samples has its flashing-point below 70° of that thermometer.'

The Abel apparatus, with a standard of 22°C., was in 1885 adopted as the legal test in Sweden, and in the year 1888 a Bill was introduced in the Danish legislature to substitute the Abel tester with a standard of 23°C., for the open tester, with a standard of 40°C., then in use in Denmark. In Russia the standard with the Abel-Pensky instrument is 28°C.

The Abel tester is by no means the only form of closed testing apparatus at present in use, and, in addition to those actually employed, a large number of instruments on the closed-cup principle have been devised. Many years ago Tagliabue, of New York, introduced an apparatus (Figs. 10 and 11) with a covered brass oil-cup communicating by means of a spring valve with a dwarf chimney. The opening of the valve and the simultaneous introduction of a flame into the chimney determines a current of air through the upper part of the oil-cup which sweeps out the inflammable vapour and brings it into contact with the flame. Tagliabue also constructed a larger instrument of the same form with a glass oil-cup. The Michigan and Wisconsin States tester has a copper oil-cup with a copper cover provided with a small orifice to which the test flame is applied. The New York State tester, devised by Elliott, has a glass oil-cup of comparatively large size with a convex glass cover. Parrish's naphthometer (Fig. 12) is provided with a stationary test flame fed by the oil in the testing cup, and Foster's automatic tester (Fig. 13) is similar in principle. In Millspaugh's closed tester (Fig. 14) the oil-cup is of glass and is immersed only to the extent of one-tenth of its depth in the water-bath, with the object, apparently, of preventing the overheating of the surface of the oil. Mann's tester (Fig. 15) represents an attempt to reproduce in the testing apparatus the conditions prevailing in an ordinary petroleum lamp, the burner of the lamp being replaced by a tube, the stopper of which is blown out when, upon the introduction of a light through a lateral opening, ignition of the vapour occurs. In Pease's closed tester (Fig. 16) the vapour is ignited by an electric-

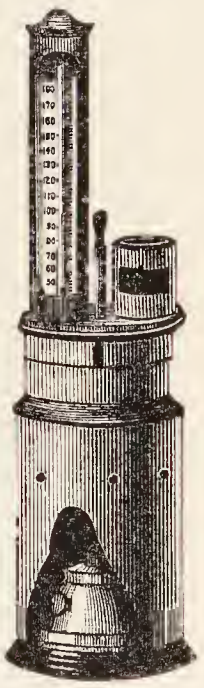


FIG. 10.

spark. The writer remembers seeing, about the year 1870, a closed tester, with electric-spark igniting arrangement, in use by Dr. Letheby in

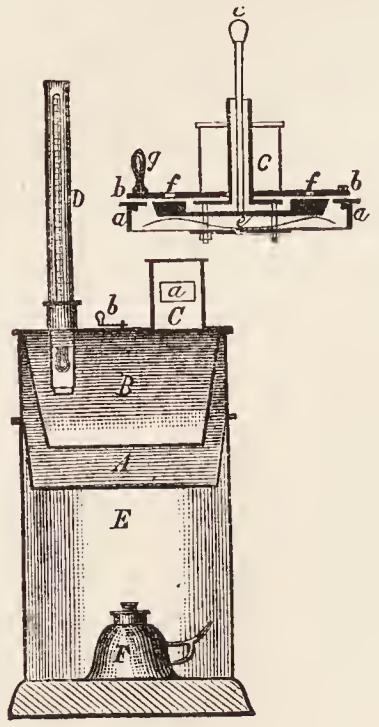


FIG. 11.

The smaller illustration represents in section the cover of the instrument shown in Fig. 10. *a*, *a*. Cover. *b*, *b*. Movable bar, with openings *f*, *f*, closed by the bar *e*, beneath which is a spring. *c*. Rod to depress the bar *e*, and thus uncover the openings *f*, *f*. *g*. Handle to move the bar *b*, *b*. C. Hood with opening for insertion of flame.

The larger illustration represents in section a simpler form of the instrument. A. Water-bath. B. Oil-cup. C. Hood, with opening *a*. D. Thermometer. E. Lamp furnace. F. Lamp. *b*. Pivoted cover, closing orifice beneath it.

his laboratory at the London Hospital. The oil-cup was of glass, with a hinged metal cover, which was blown open when the vapour ignited.

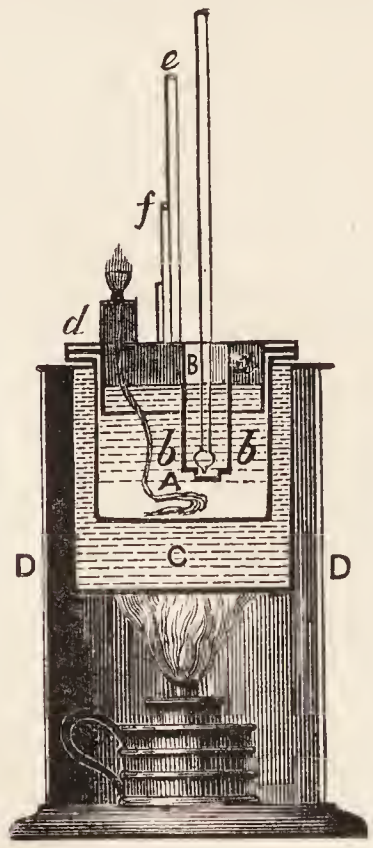


FIG. 12.

A. Oil-cup. C. Water-bath. D. Lamp-furnace. *e*. Screen, with glass plate *f*. B. Chamber communicating with the air, with openings *a* (for circulation of air) and *b*, *b* (to allow passage of oil from B into A). *d*. Cylinder supporting a small wick for test flame.

In 1882, Braun, of Berlin, patented a magnetic pendulum arrangement for applying the test flame in the Abel apparatus. In 1881, Engler and Haas made a number of experiments with the Abel apparatus and other testing instruments, and expressed the opinion that the addition of an arrangement for agitating the oil was desirable; Victor Meyer, however, previously proposed the addition of a stirrer. Owing to the facts that in the use of the Abel tester a layer of vapour of gradually increasing

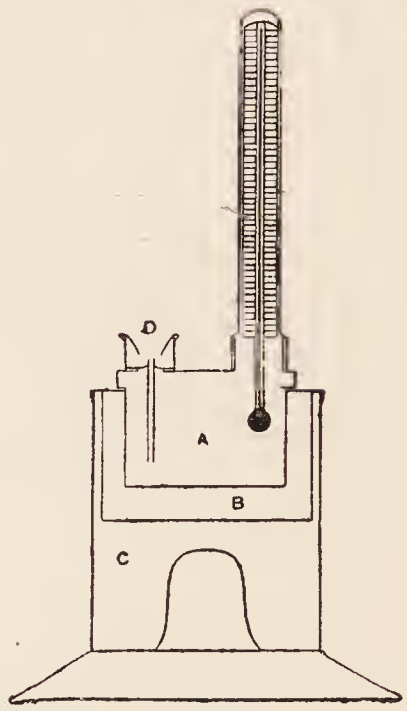


FIG. 13.

A. Oil-cup. B. Water-bath. C. Jacket. D. Flash jet.

depth is formed upon the surface of the oil and that the temperature of the oil is not uniform throughout, it is, no doubt, necessary that the dimensions of the air space above the oil, the depth to which the test-flame is inserted, the size of the test-flame, the size of the orifices in the cover, the position of the thermometer bulb, and other particulars, should be defined with greater accuracy than would probably be

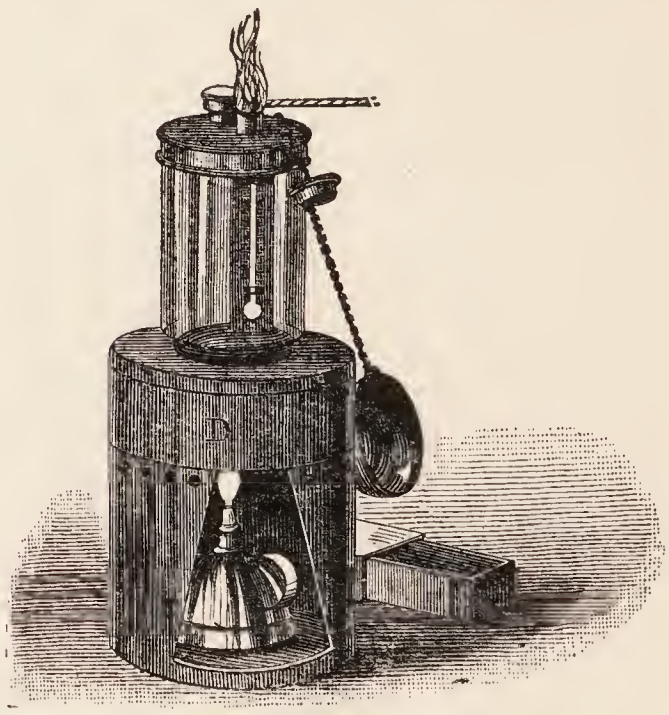


FIG. 14.

necessary if a stirrer were added, but experience has shown that the Abel apparatus can be readily standardised, and any number of instruments can thus be constructed to give concordant results if used with a reasonable amount of care. The apparatus known as the Engler tester (Fig. 17) consists of a copper water bath surmounted by a second water-bath of glass

supporting a glass oil-cup with brass cover in which are two semicircular openings with hinged lids. Two insulated wires in connection with a small induction coil terminate in platinum points 1 mm. apart at a distance of $\frac{1}{2}$ to $\frac{2}{3}$ cm. from the surface of the oil, and in the centre of

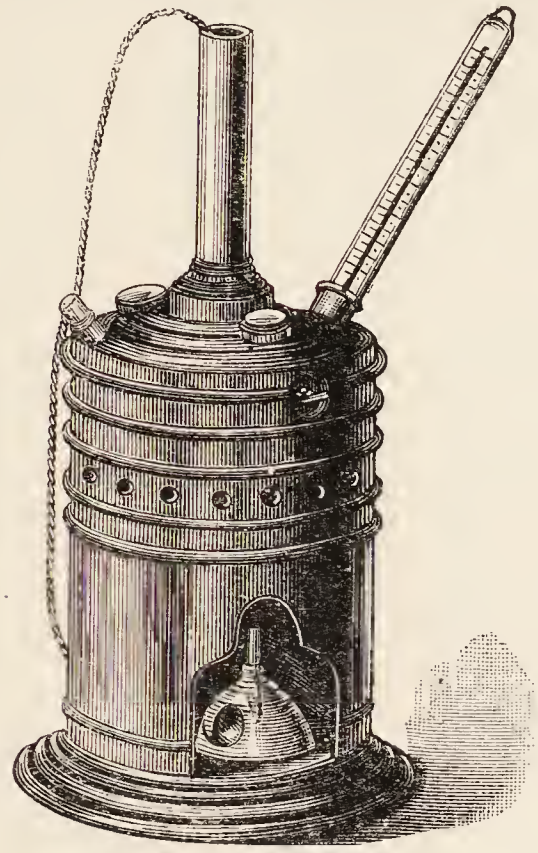


Fig. 15.

the oil-cup is a paddle stirrer attached to a spindle passing through the cover. Beneath the lower water-bath a spirit lamp is placed, and, as the temperature approaches the flashing-point of the oil, the spark is passed at each degree rise in the thermometer, care being taken that the passage of the spark is continued from half to one second. After each application of the spark the oil is gently agitated by rotating the stirrer. When the ignition of vapour occurs the hinged flaps are thrown open. It is claimed that by the use of the double water-bath and the stirrer the heating is rendered slow and regular, and as far as possible independent of the size of the heating flame; also that by the employment of the electric spark, the size, intensity, and distance of the igniting agent from the oil are rendered uniform. Moreover, that the extraneous formation of vapour through the heating of the surface of the oil which may take place when an ordinary test-flame is employed cannot occur in the use of the electric spark as described. Finally it is contended that the conditions prevailing in a petroleum lamp are reproduced to a large extent in the Engler tester.

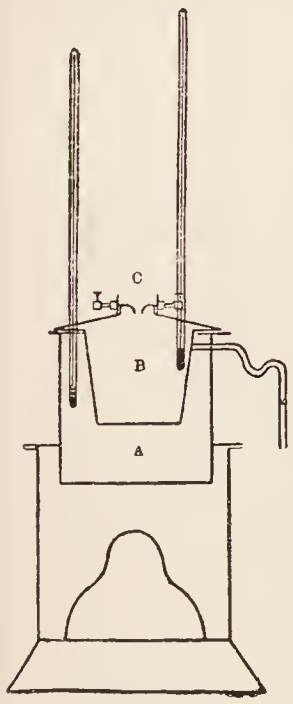


Fig. 16.

A. Water-bath. B. Oil-cup. C. Spark wires.

Among other systems of testing are those of Liebermann, Beilstein, and Stoddard, which are based upon the principle of blowing air at intervals through a jet plunged beneath the surface of the oil, contained in a vessel in which it can be gradually heated, until inflammable vapour is evolved. In Bernstein's tester (Fig. 18) the level of the oil is raised from time to time, as the temperature of the oil increases, until vapour issues from the oil chamber and ignites at a stationary flame, and in the Ehrenberg tester a syringe is employed to expel the vapour from the closed oil chamber and bring it into contact with a flame.

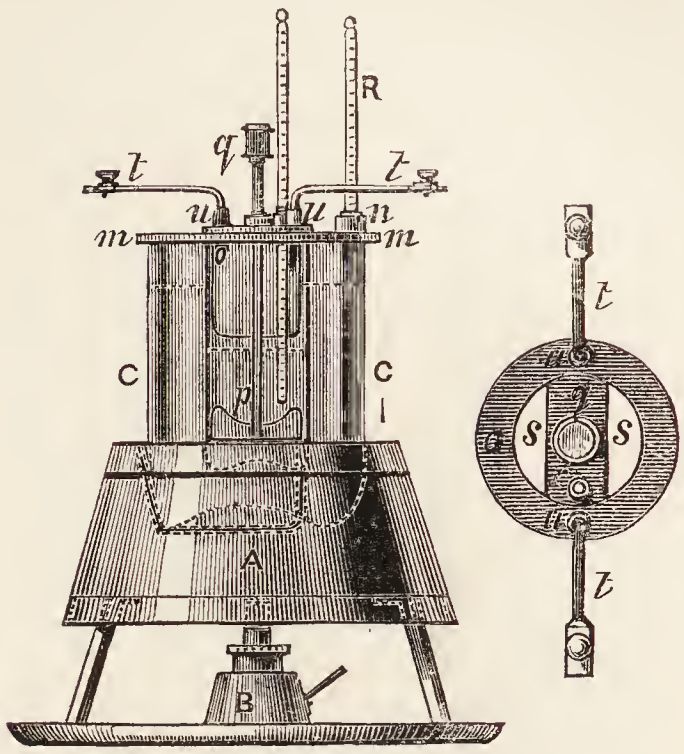


Fig. 17.

A. Copper water-bath. B. Spirit lamp. C, C. Glass water-bath, with filling mark etched upon it. *m*, *m*. Cover. R. Thermometer, supported in the water by collar *n*. *o*. Glass oil-cup, with filling mark. *s*, *s*. Openings with hinged covers. *t*, *t*. Conducting wires, insulated by ebony rings *u*, *u*, and terminating in platinum points. *p*. Stirrer, with handle *q*. *r*. Thermometer in the oil.

There yet remains to be noticed a form of petroleum testing apparatus, which has been employed to some extent in France, in which the flashing-point is deduced from the vapour tension. This apparatus, known as the Salleron-Urbain tester (Fig. 19), consists of a closed metallic vessel AA, in the cover of which are inserted a cylindrical chamber B, a regulating screw *r*, a graduated tube *m*, 35 cm. in length, and a thermometer. The cylindrical chamber is closed at the top by a screw-plug *p*, and at the bottom by a sliding plate, which cuts off communication between the chamber and the vessel below. 50 c.c. of water having been placed in the lower vessel, the cylindrical chamber is nearly filled with the petroleum to be tested, the screw-plug replaced, and the apparatus placed in

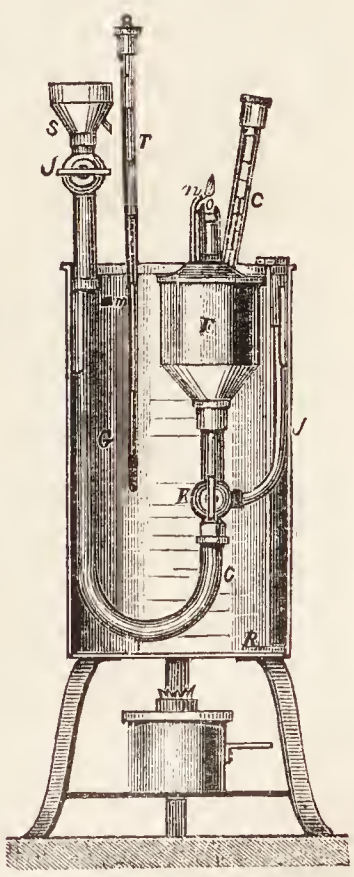


Fig. 18.

warm water until the temperature has become constant. The water-level in the graduated tube having been adjusted to zero by means

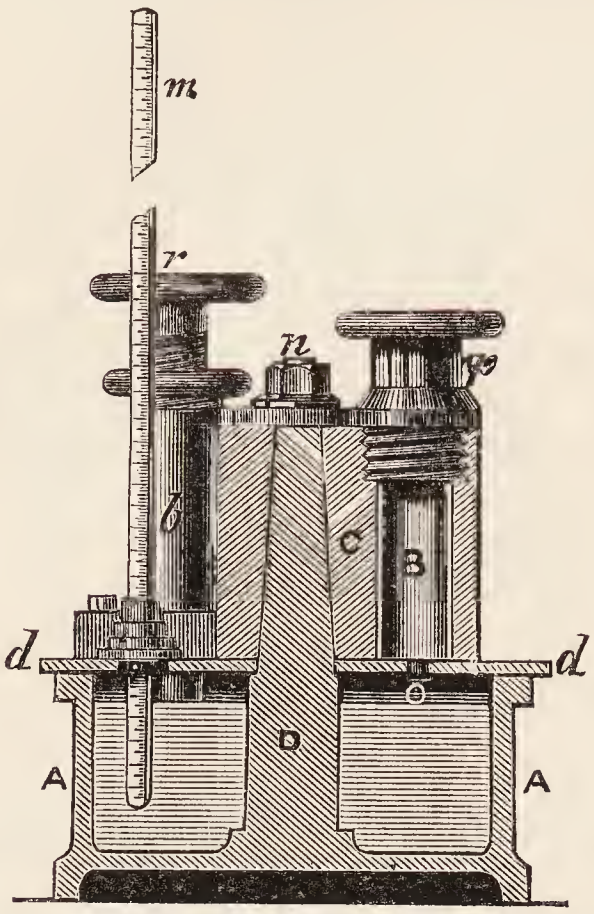


Fig. 19.

of the regulating screw, the oil in the cylindrical chamber is caused to flow out upon the surface of the water in the lower vessel by moving the sliding plate. The expansion of the liberated vapour of the petroleum causes the water to rise in the graduated tube, and, when the level is stationary, its height is read off. In a table published in 1866, Salleron and Urbain give the following figures of sp.gr. and vapour tension of petroleum at 15° :

Density at 15°C.	Tension in mm. of water	Density at 15°C.	Tension in mm. of water
0·812	0	0·756	125
0·797	5	0·735	410
0·788	15	0·695	930
0·772	40	0·680	1185
0·762	85	0·650	2110

In regard to the Salleron-Urbain system of testing, Engler and Haas remark that the method depends upon the assumption that the numbers which express the expansion of the petroleum vapour run parallel with the temperature of the inflammability of all kinds of petroleum ; but that the supposition is found not to be correct in all cases, inasmuch as the presence of a small quantity of very volatile hydrocarbons [1] occasions an increased pressure in the apparatus. The general conclusion is, however, expressed that oils which exhibit a tension of not more than 64 mm. of water at 35° may be considered safe.

In a report to the New York State Board of Health in 1882, Professor Arthur H. Elliott records the particulars of a large number of experiments with various forms of testing apparatus, and gives the following table of comparative results :—

Oil used.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
	Flashing-points, °F.										
No. 1 . . .	110°	118°	120°	111°	107°	107°	103°	130°	111°	95°	119°
No. 2 . . .	111°	121°	124°	115°	118°	109°	102°	128°	107°	96°	—
No. 3 . . .	119°	122°	122°	112°	118°	108°	102°	130°	108°	95°	118°
No. 4 . . .	97°	96°	97°	90°	93°	86°	76°	90°	81°	75°	96°

I. Tagliabue (open cup). II. Arnaboldi (open cup). III. Saybolt. IV. Tagliabue (closed cup—small). V. Tagliabue (closed cup—large). VI. Wisconsin State. VII. Abel. VIII. Bernstein. IX. Millspaugh. X. Mann. XI. Foster.

From the statements which have been made it will be evident that there is a regrettable absence of uniformity in the methods of testing adopted, not only in different countries, but also in the various States of the American Union. The existence of considerable diversity in regard to the test standard to be adopted with any one system of testing is also exhibited in the laws which have been framed in the United States. The latter condition no doubt arises from the fact that, at the outset, no systematic attempts were made to determine the relation between the flashing-point of an oil and its safe or dangerous character in ordinary use.

(*e*) *Burning quality.*—The testing of the burning quality of kerosene is regularly effected in well-conducted refineries in the United States by burning the oil in lamps of the usual construction and noting the diminution in the size of the flame which occurs in a stated period. The results are, however, dependent upon so many variable conditions that attempts have been made to substitute a test of greater precision ; but beyond the improvement of the existing test, the efforts made have not been attended with success. The Saybolt lamp (Fig. 20), specially constructed for testing purposes, consists of a tall glass cylindrical graduated reservoir of small diameter, with a burner which furnishes a well-shaped flat flame of considerable height in proportion to the width, a wick carefully selected for the purpose, and a graduated glass chimney. The lamps are burned in water at 60°F., the diminution in the height of the flame and the depression of the oil level being noted.

In Canada the ' burning percentage ' is determined by the use of a lamp thus described : ' The bowl of the lamp is cylindrical, 4 ins. in diameter and $2\frac{3}{4}$ ins. deep, with a neck placed thereon of such a height that the top of the wick tube is 3 ins. above the bowl. A sun hinge

[1] Presumably a quantity too small to affect the inflammability sensibly.

burner is used, taking a wick $\frac{7}{8}$ in. wide and $\frac{1}{8}$ in. thick, and a chimney about 8 ins. long.' The test is conducted as follows: 'The lamp bowl is filled with the oil and weighed, then lighted and turned up full flame, just below the smoking point, and burned without interference till 12 oz. of the oil are consumed. The quantity consumed during the first hour and the last hour is noted.' The ratio of the two quantities is the measure of the burning quality, and the percentage that the latter quantity is of the former is the 'burning percentage' referred to.

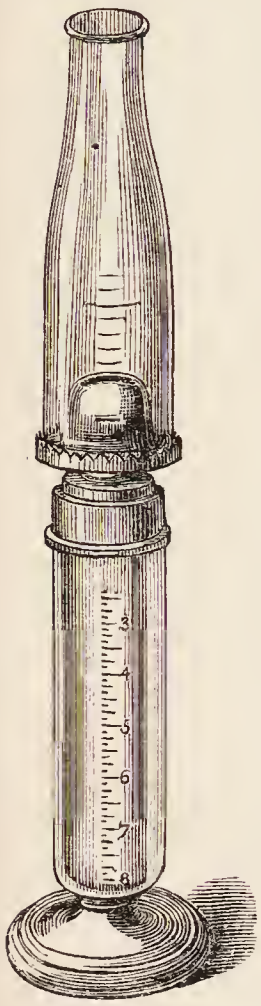


Fig. 20.

The writer has devoted much time to the perfecting of a system of testing burning quality with lamps of the usual construction, and has succeeded in eliminating some of the sources of discrepancies in the results afforded. Obviously the wick used should be carefully chosen, and, as a fresh wick should be employed for each test, it is important that the wick should be examined before use, and any defective portion rejected. In standardising the wick and verifying its uniformity, the writer has found it advantageous to determine the quantity of a mineral oil of known quality drawn out of a vessel under definite conditions as to temperature, &c., by the capillary attraction of a piece of the wick arranged as a syphon (Fig. 21). In all cases the wick must be dried immediately before use and

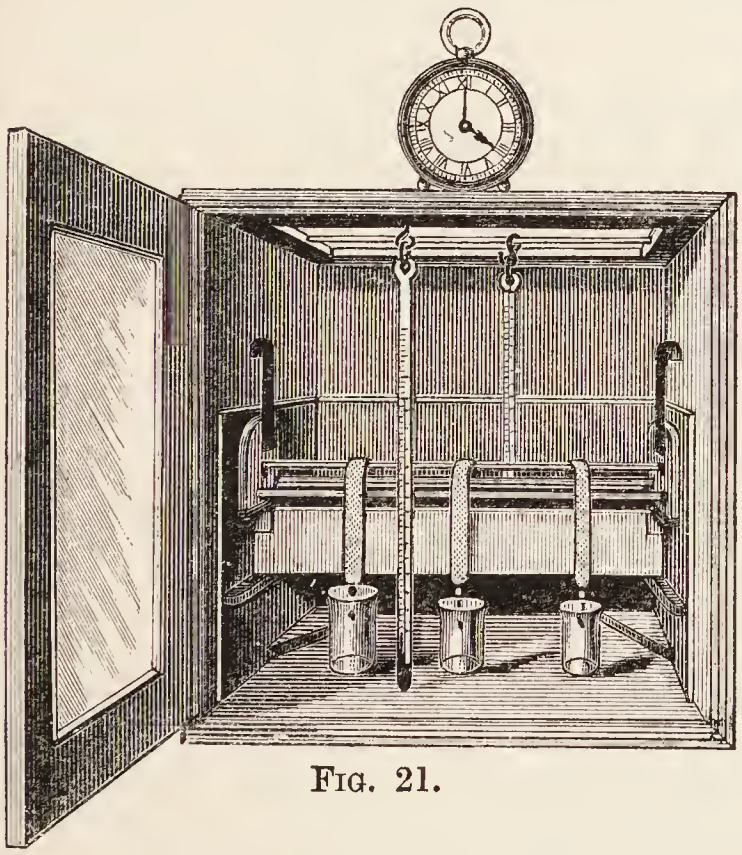


Fig. 21.

immersed in the oil while still warm. The oil chambers of the lamps employed must be of uniform dimensions, and the burners must first be tested to ascertain that they furnish similar flames with the same oil. The wick must be trimmed with scrupulous care before the lamp is lighted, and the oil in the lamp must be maintained at a constant temperature—that of 60°F. being a desirable one. The wick should be raised so as to obtain a flame of the largest size possible without the production of smoke. For recording the size and shape of the flame at the commencement of the experiment and the diminution in size and alteration in shape of the flame at intervals during the progress of the test, the writer has found it convenient to employ a camera by means of which the outline of the flame may be traced on thin paper at intervals (Fig. 22). No general agreement has, however, yet been arrived at as to the extent of diminution which shall, under the specified conditions, be permissible with oils to be classed as of satisfactory burning quality. In doubtful cases several tests of the sample should be made, as the results appear to be sometimes affected by causes not well understood. In consequence of the difficulty of devising a thoroughly satisfactory method of testing oils by burning, it has been proposed to establish a distillation test, the inferiority in burning quality being supposed to arise from the oil not being of natural composition or from its containing too large a percentage of the denser hydrocarbons. Attempts in this direction have not, however, been attended

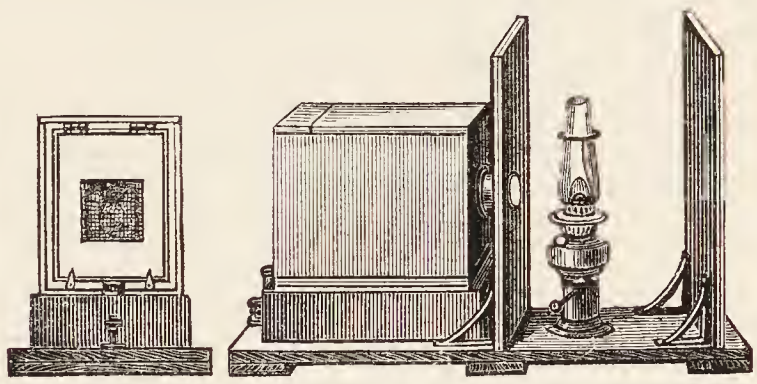


Fig. 22.

with success, oils of different burning quality furnishing in some cases similar results, and oils of equally good burning quality sometimes giving dissimilar results on fractional distillation. The testing of the oil under conditions as nearly as possible approaching to those under which it is practically used appears to be the most rational method of determining the burning quality, and is no doubt the best in the absence of any arbitrary test capable of being easily and expeditiously applied and of furnishing trustworthy results. The viscosity of the oil has been found in some cases to afford a useful indication of burning quality.

Kerosene oil should bear agitation with concentrated sulphuric acid without material darkening of colour, and warm water shaken with it should exhibit neither markedly alkaline nor even faintly acid reaction, and should give no precipitate with barium chloride solution. Upon being distilled, kerosene should not evolve sulphurous acid. If the presence of any considerable amount of sulphur compounds is suspected, the oil should be burned in a Referee's gas-testing apparatus, or in the Mahler bomb, and the sulphur products estimated as barium sulphate.

4. *Lighthouse oil.*

The Trinity House contract conditions for mineral oil intended for use in lighthouse lamps specify that—

(1) The mineral oil required to be supplied under this contract is to be of the best possible quality, the greatest care is to be taken in its preparation, and it must be perfectly free from sulphuric acid.

(2) In all cases, whether the oil be petroleum or paraffin, its flashing-point is to be determined by using the apparatus described in Schedule 1 of the Petroleum Act of 1879.

(3) If the oil be petroleum, its flashing-point is to be not lower than 125°F. (close test), and it is to distil between 302° and 572°F., the temperature of the vapour, not that of the liquid, being taken.

(4) If the oil be paraffin, its sp.gr. is to be not less than 0·810, nor greater than 0·820, at 60°F.; its flashing-point is to be not lower than 140°F. (close test), and it is to distil between 302° and 572°F., the temperature of the vapour, not that of the liquid, being taken.

(5) The illuminating power of the oil supplied, whether petroleum or paraffin, is to be equal to that of the best colza oil when consumed in a Trinity House Argand lamp.

For the distillation test about 250 grams of the oil may be taken, the operation being conducted in an ordinary distillation flask with the bulb of the thermometer midway between the shoulder of the flask and the lateral tube leading to the condenser. The upper part of the flask should be wrapped in asbestos cloth.

The United States Lighthouse establishment stipulates that mineral oil supplied for use in lighthouse lamps shall have a sp.gr. 'not less than 0·802,' a flashing-point of not less than 140°F., and a fire-test of not less than 154°F., both these tests being made with Tagliabue's instrument. The oil is to remain limpid at zero; and 'litmus paper immersed in it for 5 hours must remain unchanged.' The oil is to be photometrically tested in a fifth-order Hains lamp, and the light is to be equal to that of eighteen sperm candles, and to continue undiminished during 5 hours' burning.

5. *Lubricating oils.*

a. Colour. In the case of what are known as pale oils, the trade are accustomed to take exception to any marked increase in the ordinary depth of colour, but as yet there are no accepted standards of colour for these oils, such as have been fixed for kerosene. The writer has, however, for some years past, used the instrument (Fig. 23) known as Lovibond's Tintometer [1] in ascertaining and recording the colour of a two-inch column of lubricating oils, and comparative results have thus been furnished for the guidance of the trade.

b. Odour. Lubricating oils should be free from empyreumatic odour, as the presence of such odour would indicate that the process of refining had not been satisfactorily carried out.

c. Specific gravity. Mineral lubricating oils of similar description were formerly graded solely with reference to specific gravity, but, experience having shown that the density is not necessarily an index of the lubricating value, it is now generally recognised that specific gravity is of less importance than viscosity.

d. Flashing-point and fire-test. In the determination of the flashing-point by the closed and open tests, and for the determination of the fire-test, the writer is accustomed to use an instrument made by Pensky of Berlin. In its closed form this apparatus resembles in principle the Abel tester employed in the examination of kerosene. The water-bath is, however, replaced by an air-bath, consisting of a thick cast-iron vessel which is heated by a Bunsen burner, and the application of the gas test-flame is effected through the medium of a revolving vertical spindle with a non-conducting cap, which can be grasped by the finger and thumb without inconvenience even when the apparatus is used at high temperatures. In the use of this instrument the flame of the burner should be adjusted so that the temperature of the oil rises at the rate of about 10°F. per minute. The

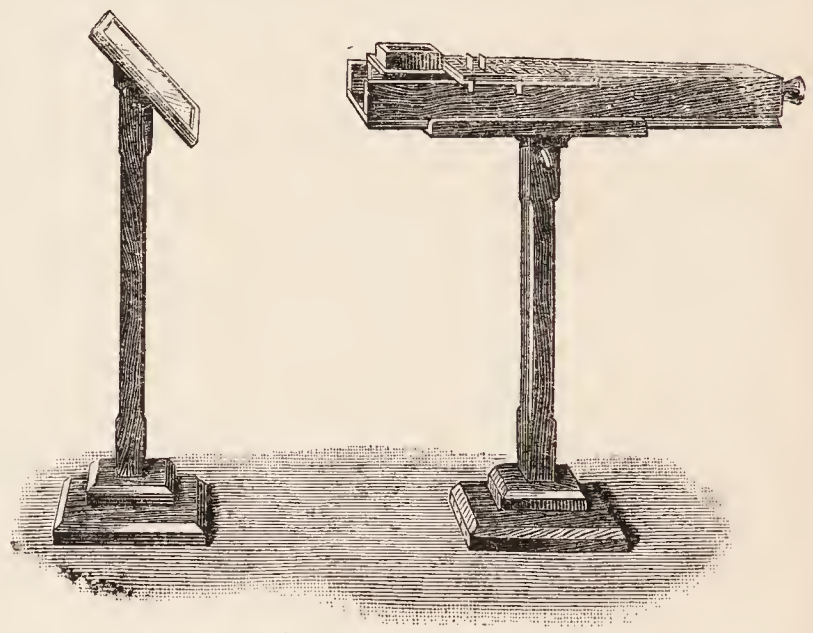


Fig. 23.

latest form of the apparatus, known as the Pensky-Martens tester (Fig. 24), is provided with a revolving stirrer which agitates the atmosphere above the oil as well as the oil itself.

If the cover of the oil-cup be removed, the apparatus referred to may be employed for the determination of the open-vessel flashing-point and the fire-test, a gas flame, not more than $\frac{1}{4}$ inch in diameter, being used to produce the ignition.

Inspectors of lubricating oils in the United States commonly use in ascertaining the fire-test an open metallic cup, supported on a tripod stand and heated directly by the flame of a spirit lamp, the temperature being raised at the rate of 8° F. per minute.

In some cases it is customary to test the volatility of the oil by noting the loss of weight sustained by a given quantity of the oil when exposed for a specified length of time in a shallow vessel to an elevated temperature. The oil is sometimes absorbed by filter-paper before exposure to heat.[1]

e. Cold-test. The method in which the

[1] This instrument, devised by Mr. Joseph W. Lovibond, of Salisbury, consists of a covered trough or box divided longitudinally by a partition terminating in a vertical knife-edge opposite an eye-piece fixed at one end, and forming two channels slightly diverging from the end at which the eye-piece is placed. In one channel the liquid to be examined, which is contained in a rectangular glass cell, is placed; and in the other channel numbered slips of coloured glass, of known depth of tint, are inserted.

[1] The writer is accustomed to expose 25 grams for 12 hours in a shallow dish to a temperature of 150°F. in the case of spindle and engine oils, and 250°F. in the case of cylinder oils.

'cold-test' of lubricating oils is made varies with the description of oil, and to some extent with the interpretation which the operator places on the term. The cold-test of pale oils is usually accepted as being the point at which on a gradual reduction in the temperature separation of solid hydrocarbons commences. To some descriptions of pale lubricating oils the following 'cold-test,' which may be termed the 'cloud-test,' is applied in the writer's laboratory: A beaker about 3 ins. in height by $1\frac{1}{2}$ ins. in diameter, is filled to a depth of 1 in. with the oil to be tested. The oil is slowly cooled, and from time to time is gently stirred with a thermometer until the first indication of the separation of paraffin is observed. This indica-

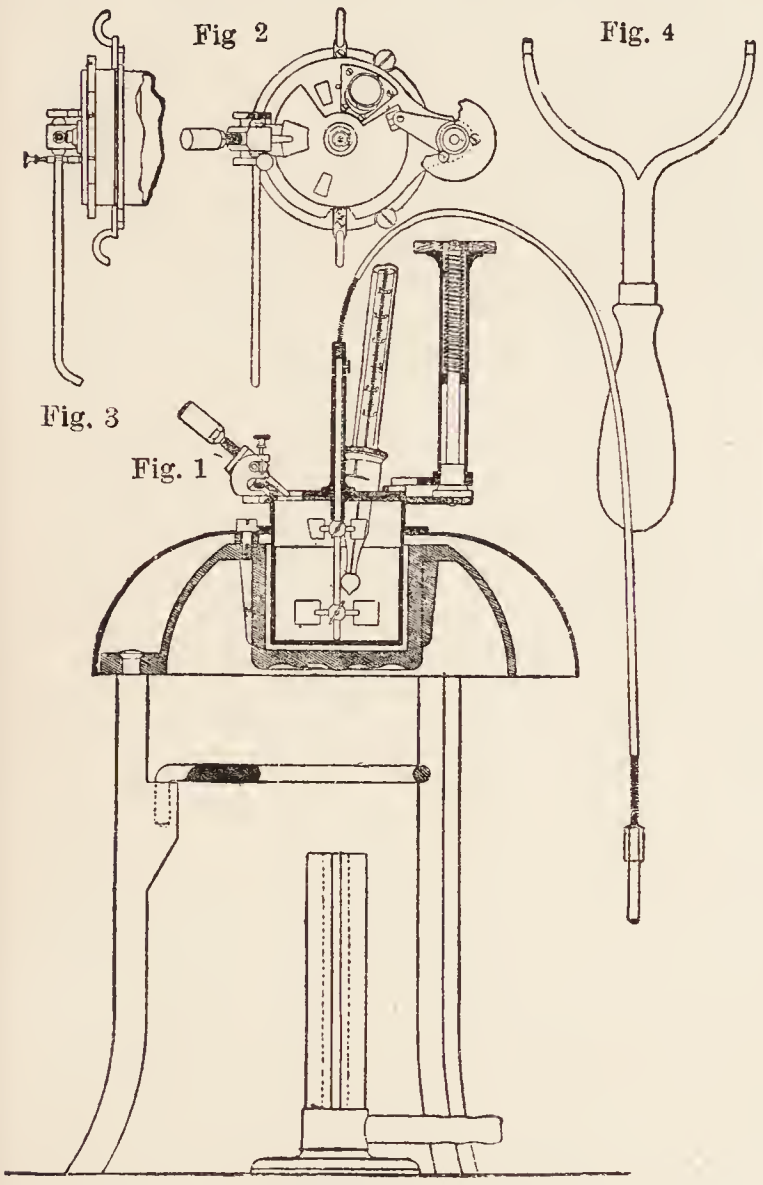


FIG. 24.

Fig. 1. Apparatus with test-flame in position for igniting the vapour. Fig. 2. Cover of oil-cup. Fig. 3. Side view of cover. Fig. 4. Handle for removing oil-cup from bath when hot.

tion often takes the form of a cloudy stream following the thermometer as it is slowly moved. Some of the more viscous pale oils contain hydrocarbons which are not very crystalline, resembling vaseline rather than paraffin wax, and the point at which these hydrocarbons begin to separate under the influence of cold is not easily determined. In some of such cases it is preferable to take the point at which the oil becomes reduced to a semi-solid consistency or ceases to flow on inclining the vessel in which it is contained. In all cases it is important that the temperature of the bath employed for cooling should not be much lower than that at which the separation, or solidification, occurs, and it is therefore desirable to determine approximately the cold-test by a preliminary operation. Where the separation of solid hydrocarbons is well defined, the test may be made in a tube about 1 in. in diameter, containing about $1\frac{1}{2}$ ins. in depth of oil in the following manner: Plunge the tube into a vessel of iced water, or, if necessary, into ice and salt, until a thin layer of paraffin congeals on the sides, stirring the oil with a thermometer while the reduction of temperature is being effected. Take out the tube, wipe it, and holding it between the operator and the window, stir the contents with a thermometer until the last traces of paraffin have disappeared, when the temperature is to be noted. Repeat the experiment, again noting the temperature. Make a third test, and if the results of the last two experiments agree, record this temperature as the cold-test of the sample.

Black oils are tested by cooling them until they cease to flow, as the commencement of

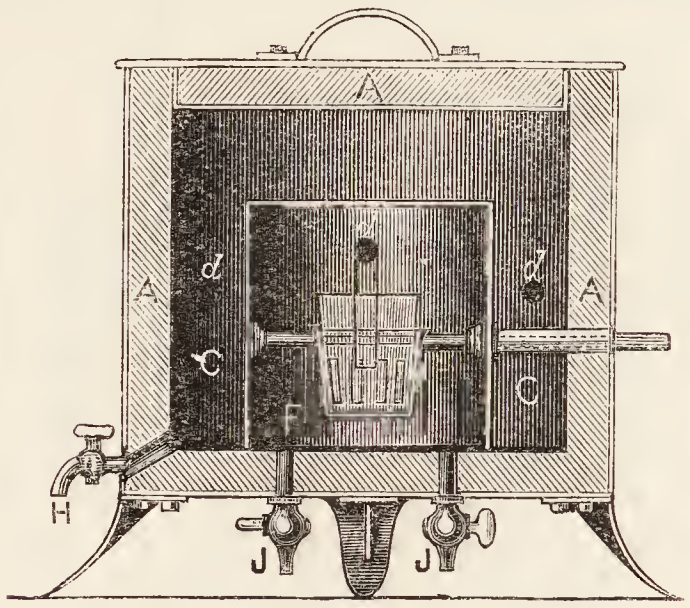


FIG. 25.

A, A, A. Non-conducting jacket. C, C. Ice-chamber. F. Oil-cooling chamber, inclosing the oil-cup, which is supported on a rocking-shaft. H. Tap for draining ice-chamber. J, J. Stop-cocks, through which warm air may be forced when it is desired to raise the temperature in F. *d*, *d*, *d*. Thermometers; the central one having its bulb in the oil.

the separation of solid hydrocarbons cannot be observed in these oils.

The rules of the New York Produce Exchange provide that the cold-test is to be determined by cooling the sample in a glass vessel, 4 ins. in depth and 3 ins. in diameter, placed in a refrigerator. A thermometer is to be placed with its bulb in the middle of the oil, and another thermometer is to be placed in the ice-chest outside the oil vessel. If, when the two thermometers both record a specified temperature, the oil is still limpid, the cold-test of the oil is deemed to be satisfactory. Tagliabue has devised a convenient form of apparatus (Fig. 25) for the application of this test, the oil-cup being supported on a rocking bar in a jacketed cooling-chamber with a glass window. In practice, however, the cold-test is usually determined by cooling the oil in a glass cylinder $1\frac{3}{8}$ in. in diameter.

f. Viscosity. It has been already stated that this test has become recognised as the proper basis for the grading of lubricating oils, and has accordingly become of considerable importance. The test is necessarily an arbitrary one,

and there is at present no universally accepted method of testing and expressing the results, though in this country the Redwood viscometer has been adopted by the Admiralty, the War Department, the principal railway companies, the Scottish Mineral Oil Association, and the petroleum trade generally. The simplest form of instrument available for the determination of viscosity consists of a glass pipette filled to a mark on the neck and allowed to discharge its contents, the relation between the period occupied in the outflow of a given sample and that required for the discharge of a similar quantity of a standard oil expressing the viscosity of the former sample in terms of the latter. The standardising of glass pipettes is, however, difficult, since the results are affected by the form of the constricted portion of the tube, apart from the size of the orifice, and two pipettes standardised with an oil of a certain viscosity may not afford concordant results with an oil of very different viscosity. Moreover, the

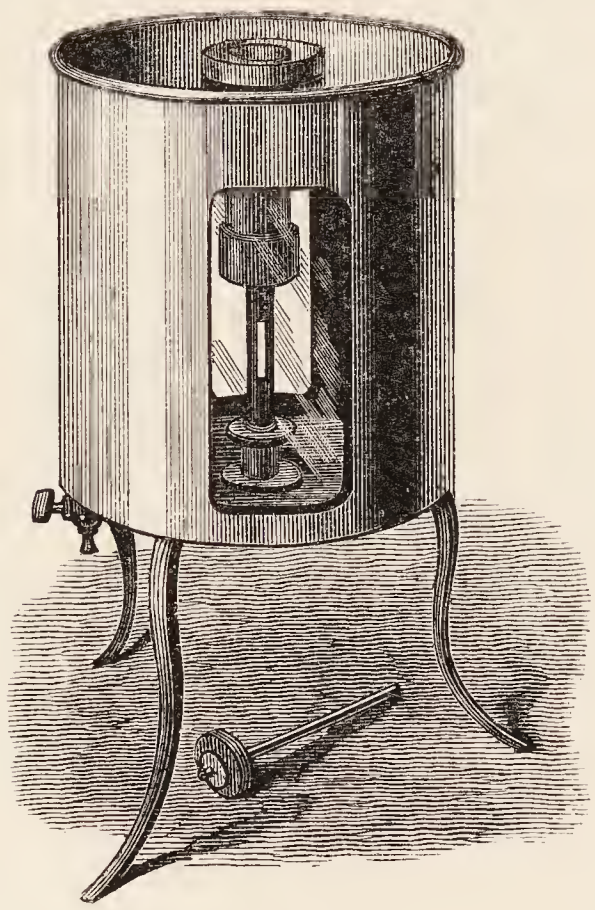


Fig. 26.

maintenance of the required temperature of a sample contained in a glass pipette cannot always be satisfactorily effected. For these reasons the jacketed glass viscometers of Veitch-Wilson, MacIvor, and Sacker have not been found to afford sufficiently accurate results.

The Saybolt viscometer, in its original form (Fig. 26), is provided with an oil vessel of comparatively large diameter placed in a water-bath of considerable capacity. The viscometer jet is of metal, and is inclosed in a tube extending below the orifice. Immediately above the jet the oil vessel is much contracted in diameter, and a portion is cut away on each side so as to expose an inner glass tube. At a corresponding level, glass windows are inserted in the water-bath. Round the upper part of the oil-vessel is fitted an oil-tight gallery with raised edge, and above the platform of the gallery the oil-cylinder is pierced with a number of small holes. In the use of the apparatus, the bath is filled with water at the required temperature, and, a cork having been inserted in the mouth of the tube inclosing the jet, the oil-vessel is filled with the oil to be tested, until overflow through the orifices referred to occurs. The oil is then stirred with a thermometer, the gallery taking the overflow, and its temperature adjusted if necessary. On withdrawing the thermometer, oil passes from the gallery into the oil-vessel to replace that which had overflowed on the insertion of the instrument. The gallery is then emptied by means of a pipette, the length of the oil column being thus determined by the position of the circle of holes; the flow of oil from the jet is started by the withdrawal of the cork from the outer tube; a stop-watch is concurrently set in motion, and the operator, looking through the window in the water-bath and through the glass tube forming the lower part of the oil-vessel, stops the watch when the oil-level makes its appearance.

The Arvine viscometer for testing cylinder oils consists of a copper tube of small diameter coiled in a bath in which water is kept in a state of ebullition. At its lower end the tube is furnished with a small stop-cock, forming a jet,

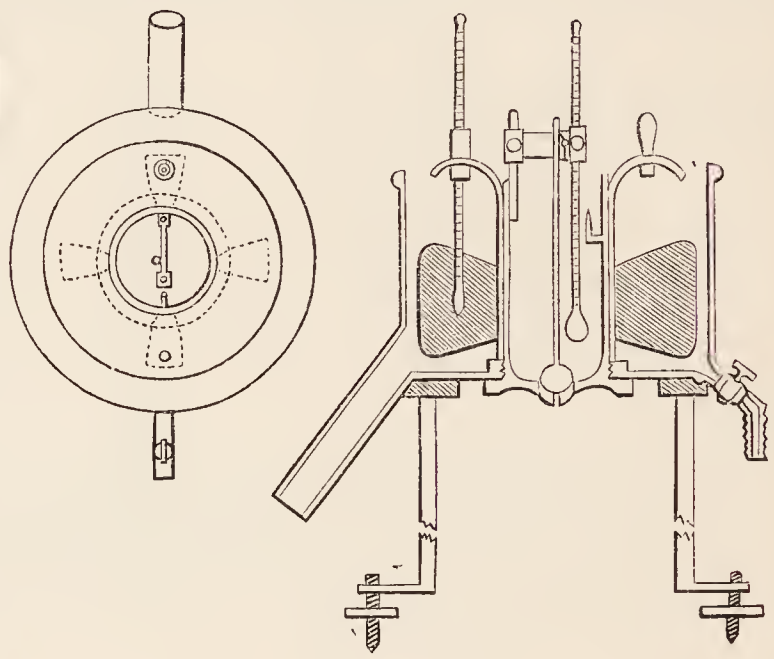


Fig. 27.

and at its upper end with a funnel to hold the oil.

The Redwood viscometer (Fig. 27) is a modification of the instrument formerly used at the Battersea Works of Price's Patent Candle Company. It consists of a silvered copper oil cylinder, about $1\frac{7}{8}$ ins. in diameter and $3\frac{1}{2}$ ins. in depth, furnished with an agate jet fitted into a slightly conical metal seating. The cylinder is fixed in a brazed copper water-bath provided with a copper heating-tube projecting at an angle of 45° from the side near the bottom, as well as with a revolving agitator carrying a curved shield to prevent splashing, and a thermometer to indicate the temperature of the liquid in the bath. The oil cylinder has a stopper consisting of a small brass sphere which rests in a hemispherical cavity in the agate jet. The sphere is attached to a wire by means of which it is raised and suspended from a standard which supports a thermometer in the oil. Inside the oil-cylinder, and at a short distance from the top, is fixed a small bracket terminating in an upturned point, which serves as a gauge of the height to which the cylinder is filled. The instrument is supported on a tripod stand. Great care is taken

in the construction of the agate jets to secure uniformity, and any slight differences in the rate of flow are corrected by slightly altering the position of the pointed bracket in the oil-cylinder. The instruments are thus all standardised. The viscometer is used in the following manner: The bath is filled with a suitable liquid to a height corresponding with the point of the bracket in the oil-cylinder. Water may be used for temperatures up to 200°F., and a heavy mineral oil for higher temperatures. The liquid being at the required temperature, the oil to be tested, which may previously be brought to the same temperature, is poured into the inner cylinder until its level just reaches the point of the gauge. A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The ball valve is then raised, a stop-watch at the same time started, and the number of seconds occupied in the outflow of 50 c.c. noted. When oils are being tested at a temperature much above that of the laboratory, a gas flame is applied to the heating tube, and the agitator kept in gentle motion throughout the experiment. The maintenance of the exact required temperature of the oil is thus, after a little practice, rendered easy. It is important that the apparatus should stand perfectly level, and that the oil should be free from dirt, water, or other suspended matter. The writer is accustomed to express the results in terms of the viscosity of rape oil at 60°F., correcting for differences in specific gravity. Accordingly the number of seconds occupied in the outflow of 50 c.c. of the oil under examination is multiplied by 100 and divided by 535 (the average time occupied in the outflow of 50 c.c. of rape oil at 60°F. according to the writer's experiments). The result is then multiplied by the sp.gr. of the oil under examination, at the temperature of the experiment, and divided by 0·915 (the sp.gr. of refined rape oil at 60°F.). It should be stated that rape oil does not take any part in the standardisation of the Redwood viscometer, and, although used in the manner described for the purpose of comparing its viscosity with that of oils under examination, 535 seconds is rather more than the time of outflow of 50 c.c. at 60°F. of rape oils of the present day.

The instrument is now so generally known and accepted that a statement of the times of outflow of 50 c.c. of an oil at given temperatures is sufficient indication of its viscosity. Several investigators have shown that the absolute viscosities of oils may be determined by the Redwood instrument.

The writer has devised a modified form of his viscometer, which, with the authority of the Admiralty, is known as the Admiralty type for testing oil fuel. This instrument, as the name indicates, has been specially constructed for use in determining the viscosity of oil fuel, for contract purposes, and is intended to be employed at a temperature of 32°F. The oil-vessel is of the same dimensions as that of the original instrument, but the agate jet is longer and of larger bore, the new viscometer being designed to give an outflow in about one-tenth of the time occupied in the outflow of a similar volume from the original pattern. The jet is so mounted as to be completely surrounded by the water in the bath. The water-bath, which is of comparatively large size, and is jacketed, has no lateral heating-tube, but is provided with the usual rotating stirrer. The design is registered, and the sole makers are Messrs. Baird & Tatlock (London), Limited. The oil to be tested should be subjected to prolonged cooling at 32°F. by being kept in a refrigerator through the night, or for at least six hours immediately before being placed in the oil-cup, which should also be cooled to 32°F. by means of crushed ice placed in the surrounding bath, and when accurate results are required the viscometer should be placed in a refrigerating chamber, the temperature of which is maintained at 32°F. The time of

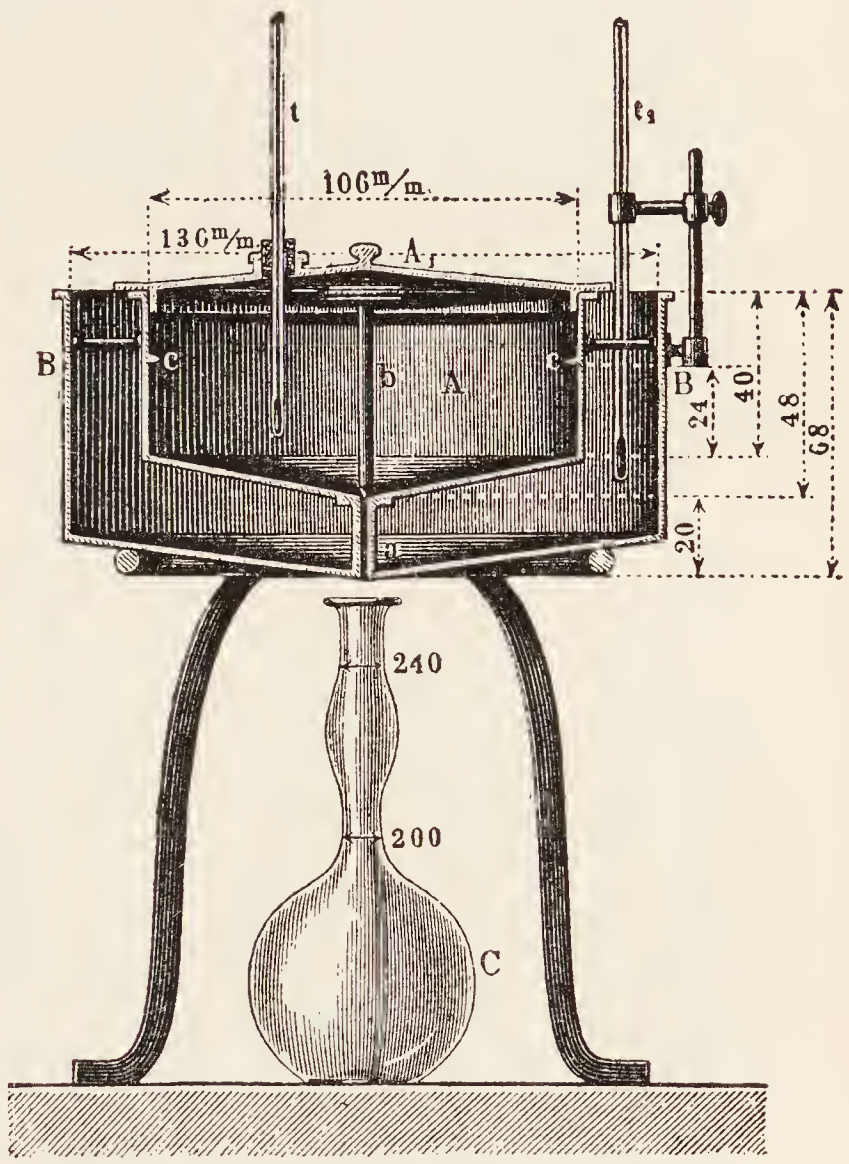


FIG. 28.

outflow of 50 c.c. of the oil is given in seconds as the Admiralty viscosity at 32°F.

The Engler viscometer, which is largely used in Germany, is constructed on the same principles as the foregoing, the viscosity of the oil being compared with that of water. The following description of the instrument is taken from the writer's 'Petroleum and its Products' (Griffin), 3rd ed., Vol. II., 278, 279:—

The apparatus (Fig. 28) is provided with an oil-cup, A, of brass, closed by a lid, A_1. The oil-cup is of the dimensions given in the figure and its inner surface is gilt. In the centre of the convex bottom of the oil-cup is an outflow-tube, *a*, of platinum (brass being attacked by the oil after being some time in use) 20 mm. long and 2·9 mm. internal diameter at the top, decreasing to 2·8 mm. at the outlet. This tube

can be closed by a pointed rod, *b*, of hard wood, introduced through the lid of the cup. Three small pointed studs, *c*, turned up at right angles, on the walls of the cup, serve to indicate the surface-level of the oil, marking a capacity of 240 c.c., and also show whether the apparatus is properly adjusted as regards level. A thermometer, *t*, is inserted in the lid to register the temperature of the oil. The oil-cup is fixed in an open oil-bath, B, containing a thermometer, t_1. The oil-bath is supported by a tripod stand, and is heated by means of a ring burner. A measuring-glass, C, marked at 200 c.c. and at 240 c.c., is placed exactly below the pipe, *a*.

To ensure the attainment of satisfactory results, the dimensions given must be strictly adhered to, for, although the error caused by altering some of them can be corrected, so far as the flow of water at 20°C. is concerned, by varying the length of the pipe, *a*, the correction is of no value for oils at other temperatures, and the difference in result between such instruments and one of standard dimensions increases with the viscosity of the oil tested.

Every instrument, even when standardised, should be tested before using the first time, and again after having been some time in use, by carefully rinsing out the cup with ether, alcohol, and water in succession, carefully drying the outflow pipe with a strip of filter paper, and observing the time required for the outflow of 200 c.c. of water maintained at 20°C. The water should be quite free from any rotary motion before the vent peg is withdrawn. The time should be 51–53 seconds, and the test should be twice repeated. The difference should not exceed 0·5 second, and the decimals of the average are counted as one second. To test oils, the cup must be most carefully cleansed of all damp and dirt, rinsed with alcohol, ether, and petroleum in succession, and then filled with the oil up to the gauge points. The oil having been brought to the desired temperature by heating the oil-bath, and maintained at that point for 2 or 3 minutes, the peg is withdrawn, and the outflow timed by a good chronometer. The result in seconds, divided by the rate for water at 20°C., gives the viscosity of the oil, *e.g.*—

Rate of flow of oil, 276 seconds.
" " water at 20°C., 53 seconds.
Result=5·2.

Oil containing suspended particles, solid matter, or water, must be filtered or dried before testing.

It has been already stated that in expressing the results obtained with the Redwood viscometer a correction is made for differences in sp.gr. As far as the writer is aware, the first published suggestion of an arrangement for eliminating differences due to sp.gr. was made by Prof. W. P. Mason, of Troy, N.Y., who described in the Chem. News for Oct. 31, 1884, an apparatus for determining viscosity, and proposed that the length of the column of the oil to be tested should be so adjusted as to be inversely proportional to the sp.gr., and maintained at this calculated length during the outflow of the standard quantity. Mr. Napier, of Glasgow, appears, however, to have previously suggested the reduction of the observed viscosity of an oil to a standard density. In the instrument proposed by Mr. Napier the oil cylinder was in two parts, connected by a flexible tube, the upper part being supported in such a manner that it could be placed at a given point on a fixed scale, the height being determined by the sp.gr. of the oil. The movable part of the oil vessel was provided with an overflow pipe, and by the use of a reservoir with a stopcock it was intended to produce a continuous slight overflow, so that the oil-level should be maintained at a fixed point.

The Mason viscometer was thus described :—

'A glass cylinder 22 ins. (55·9 cm.) long, $1\frac{1}{4}$ ins. (3·18 cm.) diameter, has a brass lower head $\frac{1}{8}$ in. (0·318 cm.) thick. An orifice is bored in the centre $\frac{1}{32}$ in. (0·794 cm.) in diameter, with bevelled edges, chamfered back $\frac{1}{2}$ in. (1·27 cm.), thus producing a sharp-edged orifice. A line marking the 18-in. (45·72 cm.) level is cut with several finer lines above and below, $\frac{1}{8}$ in. (0·318 cm.) apart, ranging from 16 to 21 ins. (40·64–53·34 cm.) above the orifice. The standard temperature is usually 60°F. (15·5°C.). A total flow of 6·103 cu. ins. (100 c.c.) is recorded by adjusting the supply so that the head shall be as nearly as possible equal to 18 ins (45·72 cm.) of water, determining this head by calculation from the sp.gr. of the oil. The rule for obtaining the viscosity is to note the time required to discharge the 100 c.c. (6·103 cu. ins.) and divide this time by that required where water under a head of 18 ins. (45·72 cm.) is used. This ratio is the measure of the viscosity.'

In the Barbet viscometer the oil under examination is caused to flow through an annular space formed by fixing an iron rod 4 mm. in diameter precisely in the middle of a brass tube 5 mm. in internal diameter. Increased resistance to the flow of the liquid is thus created, and the apparatus is stated to be more sensitive than an ordinary jet viscometer.

Lepenau's 'leptometer' (Fig. 29) consists of two similar metallic cylinders placed vertically side by side in a water-bath, and provided with three pairs of interchangeable jets to be inserted in the stopcocks at the bases of the cylinders. A standard oil having been placed in one cylinder, and the oil to be tested in the other, a pair of jets delivering the oil in drops is selected, and the number of drops falling from the two cylinders between two coincidences of dropping is noted. With dissimilar oils, however, the number of drops is not necessarily a measure of the quantity flowing through the jet, since the size of the drop varies with the nature of the oil.

McNaught's instrument for testing oils consists of two discs, the lower one provided with a raised edge and attached to a vertical spindle revolving in bearings ; the upper one resting on a pivot. The space between the two discs having been filled with the oil to be tested, the lower disc is caused to revolve at a given speed. The upper disc is prevented from partaking of the motion of the lower disc, communicated through the oil, by a projecting pin which comes into contact with a pendulum ; the extent to which the pendulum is removed from the perpendicular being the measure of the viscosity of the oil.

The paddle viscometers of Napier of Glasgow and Cockerell of Manchester are based upon the

principle of taking the speed of a paddle-wheel revolving in the oil as a measure of the viscosity. A series of concentric rings, on a vertical axis, revolving in concentric annular spaces (Figs. 30 and 31), and a hollow vertical drum revolving in a cylinder of slightly greater diameter containing the oil have also been employed by Napier. The use of a pendulum oscillating in the oil has besides been proposed. Another method of estimating viscosity which has been suggested is to note the length of time occupied in the ascent of a bubble of air through a given column of liquid, and Mills has carried out this idea by using hollow glass bulbs, but without obtaining promising results.

g. Lubricating property by direct mechanical tests. Machines have been devised by Thurston, Woodbury, Ingram and Stapfer, and others, for the mechanical testing of lubricating value. These machines are provided with accurately

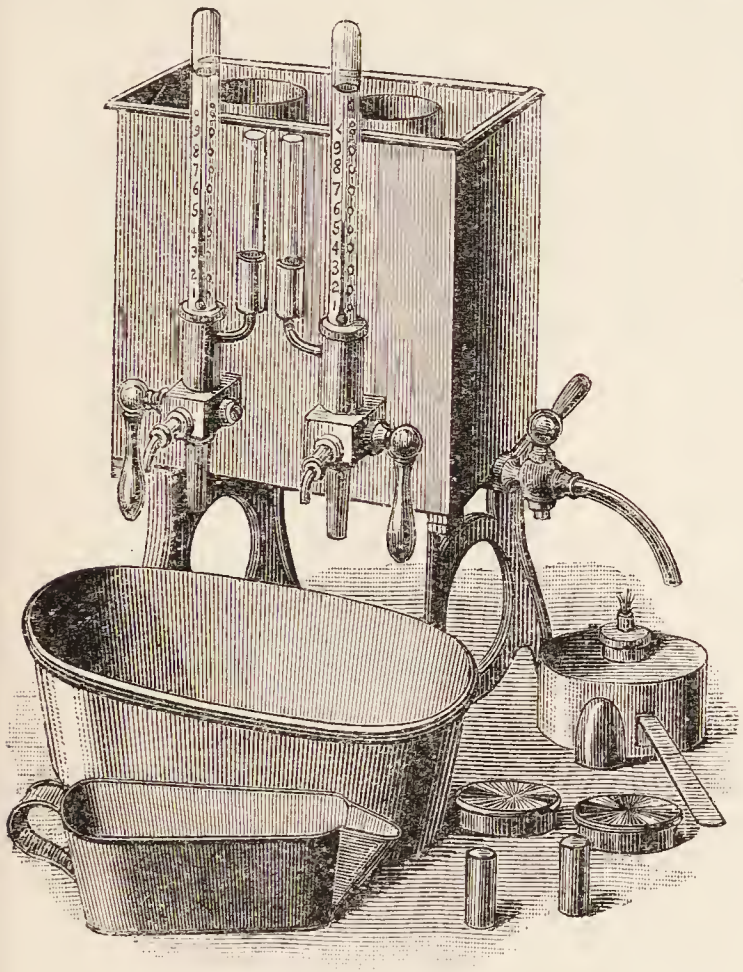


Fig. 29.

fitting fractional surfaces, between which the oil to be tested is placed, the heat and resistance at given speeds being determined. It cannot be said, however, that results of much practical utility in determining the value of lubricating oils have thus been obtained. Experience has, in fact, demonstrated that in any machine for the mechanical testing of such oils, the conditions under which the lubricants are to be actually employed must be reproduced. The writer has, therefore, been led to the conclusion that the viscosity of a mineral lubricating oil affords the best guide to its lubricating value, the consumer being thus enabled to select from time to time oils similar to those which he has found by practical experience to afford the best results in the particular circumstances of his case. This branch of the subject has been treated in some detail in a paper by the writer published in the Journal of the Society of Chemical Industry (1886, 5, 121).

h. Absolute viscosity. The generally accepted physical definition of viscosity enunciates that the viscosity of a substance is measured by the tangential force on unit area of either of two horizontal planes at unit distance apart, one of the planes moving with unit velocity relatively to the other, the space between these planes being filled with the viscous substance.

The units employed in expressing these terms are usually those of the C.G.S. system, the absolute viscosity being given in dynes per square centimetre.

It will be seen that the true or absolute

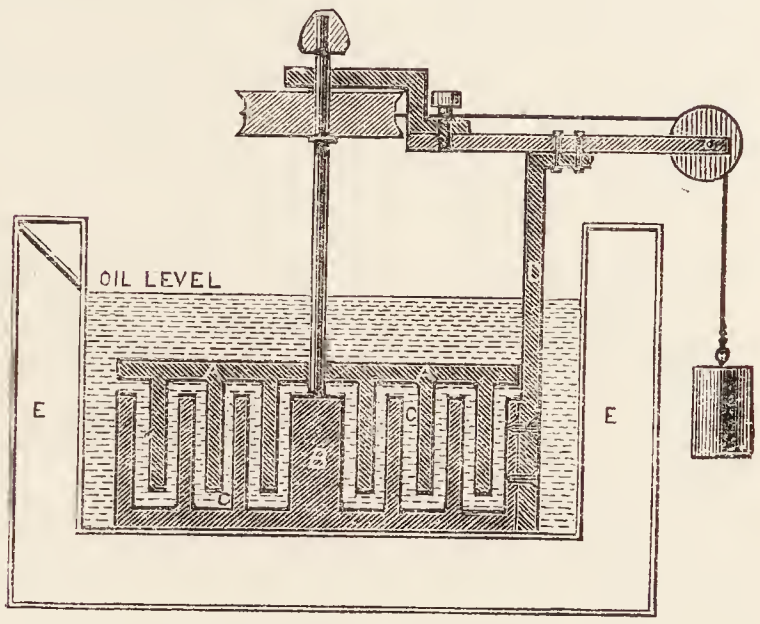


Fig. 30.—Section.

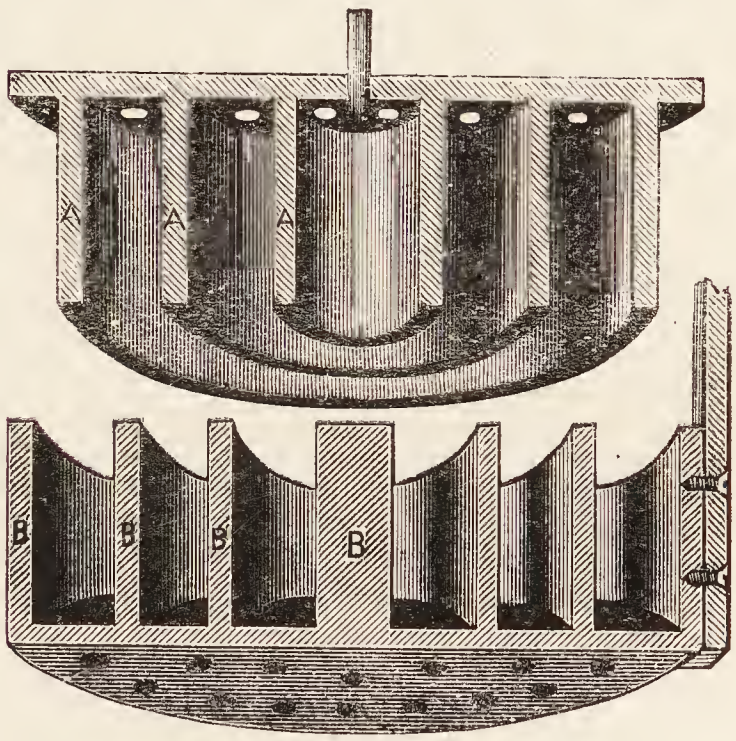


Fig. 31.—Perspective section.

A, A, A. Concentric rings, $\frac{1}{10}$ in. thick, $\frac{3}{4}$ in. deep. B, B, B. Ditto. C, C. Spaces of $\frac{1}{10}$ in. between fixed and moving rings. D. Support for driving gear. E, E. Jacket.

viscosity is quite independent of any apparatus which may be used in its determination.

The figures obtained in the use of the well-known viscometers described have a recognised commercial value, although these results, as they are generally expressed, have not the purely scientific aspect that is requisite to a consideration of true viscosity as covered by the definition. It is possible, however, to convert time of outflow as given by either the Redwood or Engler viscometer to the corresponding absolute viscosity in C.G.S. units by means of

simple formulæ based upon research work in this subject.[1]

The formula for the Redwood instrument is

$$\eta=\left(0{\cdot}00260T_R-\frac{1{\cdot}715}{T_R}\right)\delta$$

where η = viscosity in C.G.S. units,
T_R = time of outflow of 50 c.c. in seconds
δ = density of the oil at the temperature of experiment.

The formula for the Engler viscometer is based on the work of Dr. Ubbelohde, amplified by experimental investigation at the National Physical Laboratory, and is applicable to an instrument of normal dimensions having 51 seconds as the time of outflow for distilled water at 20°C.

$$\eta=\left(0{\cdot}001435T_E-\frac{3{\cdot}22}{T_E}\right)\delta$$

where T_E = time of outflow in seconds for 200 c.c.

The ratios of T_R and T_E may be calculated for any value of T_R by combining the two formulæ. The ratio $\frac{T_E}{T_R}$ for T_R=40 seconds is 1·83, and for T_R=100 seconds is 1·815; for values of T_R above 100 seconds the ratio is 1·81.

i. Purity. In the examination of mineral lubricating oils it is sometimes necessary to apply chemical tests. Oils intended for the lubrication of steam-engine cylinders should be pure hydrocarbons, saponifiable oils being liable to decomposition by the high-pressure steam, and the liberated fatty acids forming metallic soaps. The percentage of saponifiable oils present may be readily determined by treatment with alcoholic potash and extraction of the soap from an etherial solution of the unsaponifiable oil with distilled water. When a mineral lubricating oil is boiled with water and the liquids are allowed to separate, the water should retain its transparency, and should exhibit no acid or alkaline reaction. Occasionally mineral lubricating oils are adulterated with resin oil, and their viscosity is increased by the addition of aluminium palmitate or oleate, or of india-rubber. If the presence of any of these adulterants is suspected the oil should be subjected to analytical examination.

6. *Paraffin.*

a. Melting-point. The so-called melting-point of paraffin is understood in the trade to be the temperature at which the melted material begins to solidify. The two methods chiefly adopted in determining this point are known respectively as the English test and the American test. The English test is conducted by melting the paraffin in a test-tube $\frac{3}{4}$ in. in diameter, and stirring the fluid material with a thermometer while the tube is held in the air until in the process of cooling a point is reached at which the crystallisation of the hydrocarbons liberates enough heat to arrest the reduction of temperature, and the mercury remains stationary for a short time. Saybolt has devised a convenient form of apparatus for applying this test simultaneously to several samples, the melted material being contained in a series of parallel troughs mounted on a carriage so as to travel backwards and forwards, the thermometers being held rigidly above the troughs in a frame in such a position that the bulbs are just immersed. The American test is made by melting enough of the material to three-parts fill a hemispherical dish about $3\frac{3}{4}$ ins. in diameter, allowing the paraffin to cool in the air and noting the temperature at which a very thin film extends from the sides of the vessel to a thermometer with a round bulb half an inch in diameter suspended in the middle of the dish so that the bulb is only three-fourths immersed. The melting-point by the American test is usually from $2\frac{1}{2}$°–3°F. higher than that indicated by the English test. Some operators prefer to note the temperature at which a minute quantity of the sample, previously fused into an open capillary tube (care being taken not to overheat the material) and allowed to solidify, becomes fluid when the tube is allowed to warm slowly by the side of a sensitive thermometer in a beaker of water.

b. Percentage of oil. The determination of the percentage of oil in paraffin scale is a purely arbitrary test, as there is no natural line of demarcation between the solid and liquid hydrocarbons of petroleum. The test is made by subjecting the material to pressure and noting

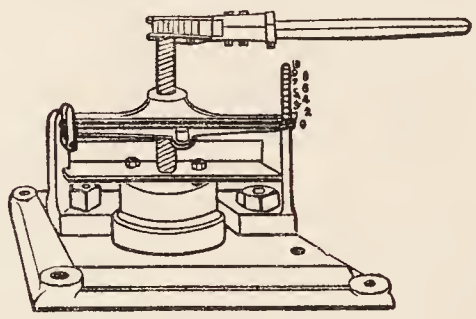


Fig. 32.

the loss in weight, but the results obtained depend upon the temperature at which the operation is conducted, the quantity of material in relation to the diameter of the press-cake and the amount and duration of pressure. The writer had some years ago a press (Fig. 32) constructed for the purpose with a steel crosshead, the deflection of which was magnified by levers, and the amount of pressure applied was thus indicated, and he now makes use of a press (Fig. 33) wherein a heavily weighted lever is used to regulate the pressure. Both these presses are provided with circular press-cups and plungers $5\frac{5}{8}$ ins. in diameter, and the pressure employed in testing American paraffin scale is 9 tons on the total surface. The quantity of material operated upon is 500 grains, and the pressure is applied for 5 minutes at a temperature of 60°F. The paraffin is placed between circular pieces of calico cut with a steel punch to fit the press-cup, and the oil expressed is absorbed by a sufficient number of discs of blotting-paper placed above and below the cloth containing the cake. The temperature of the press-cup and the plunger is indicated by thermometers inserted in mercury-cups, and the paraffin is also brought to the standard temperature before being pressed. The testing press designed by McCutchon (Figs. 34 and 35) is furnished with a helical steel

[1] National Physical Laboratory, Collected Researches, Vol. XI. pp 1–16.

spring, the extent of compression of which indicates the amount of pressure applied. Messrs. Clarkson and Beckitt, of Glasgow, have made an excellent hydraulic press (Fig. 36) for the purpose, which occupies less space than a lever press.

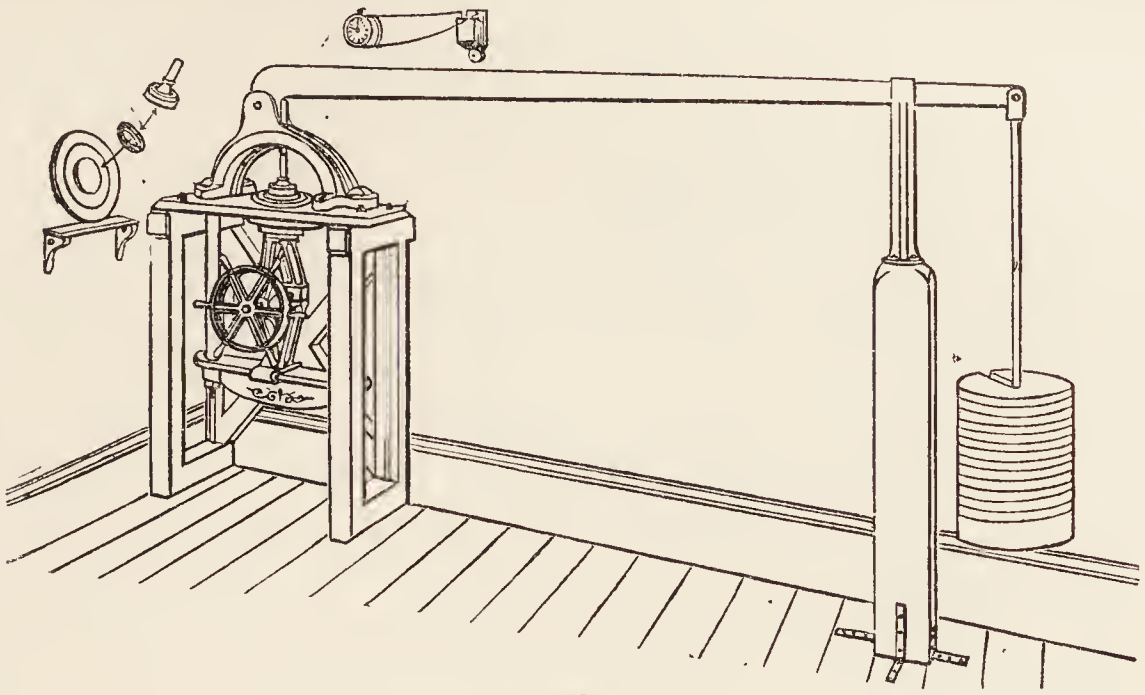


FIG. 33.

c. Percentage of water and dirt. The percentage of water in paraffin scale may be determined by heating a weighed quantity in an

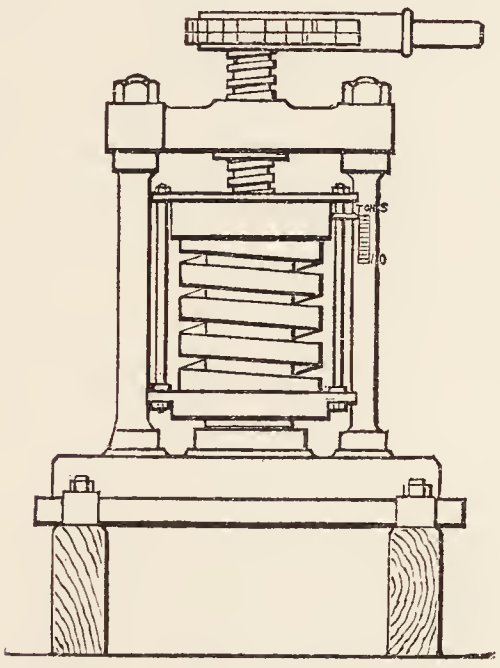


FIG. 34.

evaporating dish to a temperature somewhat above the boiling-point of water, the melted paraffin being continuously stirred until the

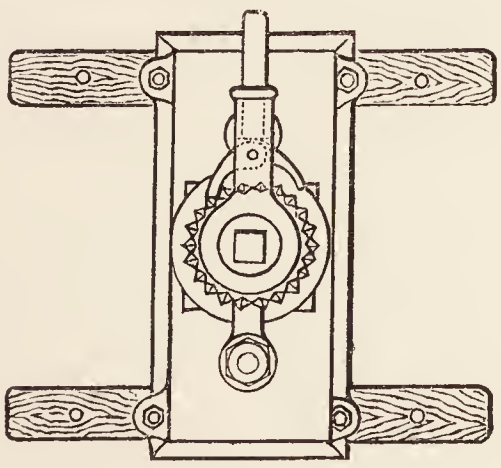


FIG. 35.

whole of the water has been driven off, when the loss in weight is noted. If the quantity of water present is large the percentage may be determined by distillation or by subsidence, the paraffin being retained in a melted state until the water has separated. Sutherland [1] has introduced a convenient form of apparatus for making the latter test, consisting of a bulbed tube (taking a charge of 50 grams of paraffin) the lower part of which is graduated. In the use of this instrument the greater portion of the melted paraffin may be readily poured off by removing the tube from the heating-bath when the water has separated, and plunging the lower end into

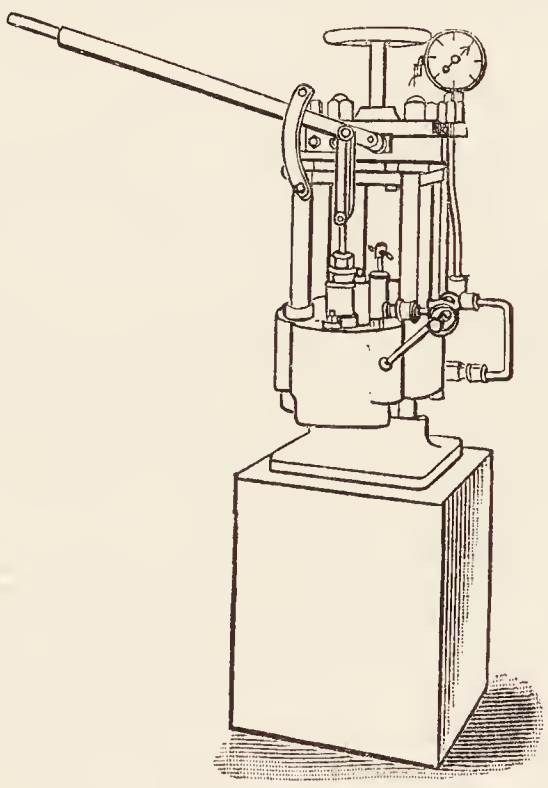


FIG. 36.

cold water so as to seal the water by causing the solidification of a layer of paraffin above it. The operation may then be completed by dissolving the remaining paraffin in warm petroleum spirit (hydrated). In this method of testing the dirt is usually estimated with the water, but if the proportion of dirt is considerable it should be collected on a filter paper, washed with mineral spirit, dried and weighed.

The following methods of testing Scotch

[1] J. Soc. Chem. Ind. 1887, 6, 123.

paraffin scale and heavy mineral oils were agreed upon by the chief chemists of the Scottish Mineral Oil Association, Price's Patent Candle Company, and the writer.

1. Scale Analysis.

1. *Sampling of hard scale.* The sample is to be taken by means of a metal tube, which is made slightly conical; the small end is inserted in the scale, and by means of a handle, which is removable, it is forced through the scale to be sampled. By this means a cylindrical core of paraffin is obtained.

Care must be taken to see that the tube is of such a length that the sample will represent the whole length or depth of the cask, waggon, or bing.

2. *Preservation of samples of scale.* Immediately after the sample has been drawn it is to be thoroughly mixed, placed in suitable wide-mouthed bottles, which may be closed either with glass stoppers or good corks; if the latter are used, they should be covered with paraffin paper or soaked in melted paraffin wax before being inserted. The bottles are then finally sealed in the usual manner. The scale should be tightly packed into the bottles, which should be completely filled.

3. *Determination of oil in scale.* (a) *Press to be used.* While no one special form of press is recommended for general adoption, the press used must have some arrangement for indicating the pressure applied. The cup in which the scale is placed during the application of pressure to have an area of 20 sq. ins.

(b) *Preparation of the sample.* A quantity of the scale, after having been freed from water and dirt by melting and subsidence, is to be allowed to cool over night to a temperature of 60°F. The solid mass is then ground to a fine powder, a portion of which is used in the determination of the oil.

(c) *Quantity of scale to be used.* The quantity of scale to be used in the determination of oil is to be 250 grains, which quantity may, however, be reduced to 150 grains in the event of the scale containing much oil (over 7 p.c.). With 'soft' scale the smaller quantity should be taken.

(d) *Temperature at which the scale is to be pressed.* The temperature of the scale and the press is to be 60°F.

(e) *Time during which the scale is to remain under pressure.* The scale is to remain under pressure for 15 minutes.

(f) *Pressing cloths and papers.* Fine linen pressing cloths and a number of layers of filter-paper, sufficient to absorb all the oil, to be used. The exterior papers must not be soiled by oil.

(g) *Pressure to be applied.* The maximum pressure is to be 10 cwt. per square in. and the working pressure 9 cwt. per square in.

4. *Determination of water in scale.* The amount of water present in scale may be determined by either of the following processes:

(a) Distillation from a copper flask. From 1 to 2 lbs. of the scale are heated in a conical copper flask of about the dimensions shown in the annexed sketch; this is connected to an ordinary Liebig condenser. By means of a powerful Bunsen burner or lamp, the water, accompanied by a small quantity of light oil, is volatilised and condensed. The distillate is received in a narrow graduated measure, so that the volume of water can be readily ascertained. As a little water usually adheres to the sides of the condenser tube, this is to be washed out with hydrated gasoline or naphtha and added to the principal quantity.

(b) Price's Company's method. 500 grains of the scale to be tested are weighed in a tared porcelain basin and heated with constant stirring to 230°F. until bubbles cease to be given off; the loss is then determined.

500 grains of the same scale, which has been freed from its water and dirt by melting at a gentle heat and subsidence, are to be heated in the same way, to a similar temperature, and for the same time, and the loss again determined. The loss in the second instance is now to be deducted from the loss found in the first experiment, and the remainder is then to be taken as the quantity of water present.

5. *Determination of dirt in scale.* The amount of dirt present in scale is to be determined by melting a weighed quantity of the scale and, after subsidence, pouring off the clear paraffin. The residue is then mixed with naphtha,

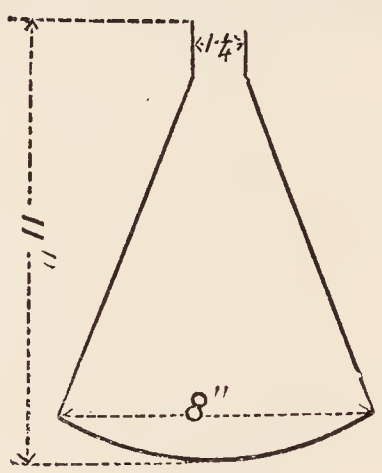


Fig. 37.

thrown on a weighed dry filter-paper, washed with naphtha or gasoline, dried and weighed. When available, the quantity of scale to be used in the determination of the percentage of dirt should not be less than 7000 grains.

6. *Calculation of the results of the analysis of scale.* As the oil is determined on scale which has been freed from water and dirt, the result must be calculated back to the original scale containing water and dirt.

7. *Determination of the melting (setting) point of solid paraffin.* This is to be determined by what is known as the 'English' test, *i.e.* a test-tube about 1 in. in diameter is filled to the depth of about 2 ins. with the melted paraffin, a small thermometer is inserted, and the whole steadily stirred, while the test-tube and its contents are allowed to cool slowly. The temperature at which the thermometer remains stationary for a short time is the melting (setting) point.

II. Flashing-point of Heavy Mineral Oil.

8. *Determination of the flashing-point of heavy mineral oil.* The oil-cup and cover of the ordinary 'Abel' flash-point apparatus are to be employed. The cup is filled with oil in the usual manner, and the rate of heating is to be

such that at least 15 minutes are taken in raising the temperature of the oil to 300°F. In the event, however, of a dispute arising as to the correct flashing-point of a heavy mineral oil, the question is to be decided by means of the 'Pensky-Martens' apparatus (J. Soc. Chem. Ind. 8, 734).

III. Viscosity of Mineral Oil.

9. *Determination of the viscosity of mineral oil.* The instrument known as the 'Redwood' viscometer is that which is to be employed in the determination of the viscosity of mineral oils. The instrument is to be standardised according to the directions given by Mr. Boverton Redwood (J. Soc. Chem. Ind. 5, 127). Ordinary results are to be expressed, as the time in seconds which 50 c.c. of the oil take to flow through the orifice at a temperature of 70°F.

IV. Setting-point of Mineral Oil.

10. *Determination of the setting-point of mineral oil.* This is determined in the following manner. Into a test-tube having a diameter of about 1¼ ins. the oil to be tested is added to the depth of about 2 ins.; the tube is then immersed in a freezing mixture, the oil being slowly stirred with a thermometer until it is cooled down considerably below the temperature at which solid paraffin first appears. The tube is then removed from the freezing mixture, the oil constantly stirred with the thermometer, and the point carefully watched at which the last trace of solid paraffin disappears. This operation is repeated with the same sample of oil until two experiments give concordant results, the temperature so found being the setting-point.

7. *Oil fuel.*

Although the world's annual output of petroleum is relatively small in comparison with that of coal, and consequently insufficient, even after making all allowances for possible increase of production, for oil fuel to attain the position now held by coal as a fuel for general purposes, there are, undoubtedly, certain classes of employment where the liquid fuel has obvious advantages over the solid form. For example, the superiority of oil for naval purposes is emphasised by a consideration of the following facts:—

(*a*) Economy of space reserved for carrying fuel.

(*b*) Ease in taking in fresh supplies.

(*c*) Rapidity of time in meeting variable load on boiler.

(*d*) Ability to force the boiler to extreme duty in case of emergency.

(*e*) Absence of smoke under light normal working conditions.

(*f*) Short height of smoke stack.

(*g*) Saving in labour.

(*h*) Superior personnel available for the operation of the burners.

(*i*) Ability to secure and maintain higher speed with oil fuel than with coal.

The advent and subsequent successful development of internal-combustion engines of the Diesel type have brought oil fuel to the fore as a highly valuable source of power on land and sea, by increasing the efficiency of the conversion of thermal to mechanical units.

Crude petroleum is frequently used on the various oil-fields for steam-raising purposes, but, in view of the inherent risks of utilising for such purpose oils which contain the more volatile hydrocarbons, it is necessary to remove these compounds by distillation where storage and transportation of the oil are involved, in order that the fuel produced shall have a specified minimum flashing-point. This minimum flashing temperature is usually prescribed by law, and varies between the approximate limits of 140°F. and 200°F. in different countries.

Apart from this condition there are others with which the oil fuels should comply, the more important being low sulphur content, freedom from solid hydrocarbons at low temperatures, absence of dirt and other suspended impurities, and a maximum limit to the permissible amount of water.

Oils intended for use as liquid fuel should be examined also for specific gravity, free acidity, asphaltic matter, and calorific value.

Calorific value. This is best determined by burning one gram in a bomb calorimeter of the Mahler or similar type. Accuracy to within about half of 1 p.c. may be obtained with careful working.

Sulphur. After the determination of the calorific value, the gaseous products of combustion in the bomb are led through a slightly alkaline scrubber, the liquid in which is added to the rinsings of the bomb and the whole precipitated with barium chloride in the usual manner.

8. *Gas oil.*

An important commercial value is attached to the utilisation of petroleum for the manufacture of carburetted water-gas.

Some of the intermediate distillates of petroleum, and especially gas oil (Solar oil) are of particular importance under this heading.

The process consists of three stages, in the first of which 'water-gas' is generated by passing steam through a bed of incandescent coke. The gas then passes to a second heated chamber, into which gas oil is sprayed over chequer brickwork. The oil is vaporised and the mixture of gas and vapours then passes to a third chamber, which is maintained at a higher temperature, and here the oil vapours are converted into permanently gaseous hydrocarbons by 'cracking.'

The resulting mixture of gases has a high illuminating value and affords to the gas engineer a means of meeting sudden demands for illuminating gas caused by fog or dull weather, owing to the readiness with which carburetted water-gas mixes with the gas obtained by carbonisation of coal.

Gas oils are tested for specific gravity, flash-point, sulphur content, asphaltic content, and freedom from water and dirt. In some cases a distillation test, designed to secure uniformity in the oils supplied, is also carried out.

'Cracking' of petroleum. The products yielded by the pyrogenetic decomposition of the more complex compounds of petroleum are of considerable economic and commercial

importance and may be divided into five main classes, viz. :—

(1) Permanent gas.
(2) Illuminating oils.
(3) Aromatic hydrocarbons.
(4) Distillate fuels for engines of the internal-combustion type.
(5) Diluents for viscous petroleum residues.

The development in connection with the use of petroleum has brought about the necessity of treating the heavier constituents of petroleum to produce more serviceable products.

As previously stated, the gaseous products form a valuable agent for the enrichment of coal-gas and for other means of furnishing gaseous illuminants and sources of power.

Illuminating oils are increased in yield by a judicious control of the direct distillation of the crude oil, and, by a more intensive treatment, decomposition of the higher-boiling constituents results in the formation of members of all the homologous series of hydrocarbons in proportions varying according to the method of treatment, the volatility of which is greater than that of the oil from which they are derived.

Thus, the potential sources of the five classes of products enumerated are greatly increased, and promise to go some way in the direction of meeting the rapidly increasing demand for these important bodies whose value depends upon volatility or other useful property.

The following are brief particulars of the principal methods adopted for the cracking of petroleum residues. A large number of patents have been granted for other processes which are less important because they do not appear to have been exploited to the same extent as those to be described.

The *Burton* process is in extensive use in the United States by the Standard Oil Company. There is some doubt as to the reasons for granting a patent for this process, because the operations are precisely similar to those patented by Dewar and Redwood in 1889, viz. the distillation and condensation were carried out under pressure. It is true that these operations were devised to produce larger yields of kerosene, that product being much more important than motor spirit at the period of the granting of the original patent, but the apparatus devised by Dewar and Redwood would give similar results to those which are being obtained with the Burton process. The Burton plant and process are used at temperatures ranging from 350°F. to 450°F., the less volatile petroleum residues being distilled at these temperatures at a pressure of 4–5 atmospheres maintained throughout the plant by means of valves placed at the outlet of the condenser.

The *Rittman* process for the manufacture of motor spirit and aromatic hydrocarbons from petroleum was granted letters patent in England in 1915.

The discovery of the process and the subsequent development of the large-scale operations resulted from investigations conducted under the auspices of the U.S.A. Bureau of Mines.

Rittman is of opinion that gasoline formation begins at about 400°C., reaching a maximum at 500°–550°C., whilst the maximum yield of benzene-toluene is furnished between the temperature range 650°–700°C.

The plant, as finally adapted for the commercial production of benzene-toluene, consists of six furnaces, each containing two rows of five vertical cracking tubes (11½ feet long and 8 inches diameter) which are heated by twenty-two gas burners. Each tube has its own separate oil supply and separate condenser. The carbon deposited on the interior walls of the tubes is removed by a rotating rod passing axially through each tube, and having chains attached spirally, the carbon being collected in carbon pots specially provided for the purpose. The cleaning device is only effectual for a few days, and then has to be removed for cleansing.

The oil supply is fed at 15 gallons per hour for benzene-toluene, and for gasoline (motor spirit) at twice that rate, and pressures of about 10 atmospheres are employed.

The products are led from the converter tubes down a pipe slightly inclined towards a primary separator, where the heavier products are collected and run off, the products still in a vaporous state being conducted by a swan-neck pipe to the condenser and secondary separator.

The gas produced is of high calorific value (approximately 1200 B.Th.U. per cu. ft.), and more than sufficient is obtained when the plant is 'run' for benzene-toluene to maintain the gaseous fuel supply to the burners, but when 'run' for gasoline the plant is not self-supporting in this respect.

The following figures are yields claimed for the process :—

Benzene-Toluene Operation.			*Gasoline Operation.*	
Benzene	6–8 p.c.		Gasoline . .	25–30 p.c.
Toluene	6–8 ,,		Residuum above 150°C. . .	70–73 ,,
Creosote Oil and Pitch	25–30 ,,	of the original oil.		
Carbon	3–5 ,,			
Gas	45–60 ,,			

The Rittman process is necessarily an intermittent one, in view of the fact that the cleaning device requires dismantling fairly frequently, with the consequent delays in operating arising from this cause, and, presumably, also from the cooling and heating of the brickwork setting. A feature peculiar to the process is the comparatively large diameter of the 'cracking'-tubes.

Another process, due to Hall, who took out a patent in 1913, has been in operation for the production of aromatic hydrocarbons and of motor spirit by the pyrogenetic decomposition of petroleum, with favourable results. Briefly, the present method of carrying out the process is as follows : The oil to be treated is fed in at the cooler end of a continuous coil of approximately 600 feet of cold-drawn tubing 1 in. in internal diameter, heated to a temperature which varies according to the desired product, but which can be maintained within a few degrees of that temperature for several hours. The pressure, which ranges up to 110 lbs. per sq. in., is also varied to suit the product required, and is easily controlled at any pre-determined figure. The oil, fed in at the cooler end of the coil, becomes heated and vaporised during its passage through the tubes, the vapours at the latter end of the coil having a high velocity,

and at this part of the coil they encounter the highest temperature. At the exit of the 'cracking'-tubes the vapours are suddenly expanded to atmospheric pressure into a tube of much larger diameter. It is at this part of the plant that most of the cracking reactions take place, and graphitic carbon is formed. An appreciable rise of temperature without external aid is experienced here, due partly to transformation of the kinetic energy of the high velocity of the vapours into heat, and partly to molecular disruption of the oil. The vapours now pass through dephlegmators of the Raschig type; pitch and a small quantity of spongy carbon separate in the first dephlegmator, in the second a heavy oil residue free from pitchy matter, and in the third one a mobile and volatile residue.

The vapours, now cooled to about 100°C., are conducted to compressors, and they are compressed, cooled, and stored under 50–75 lbs. per sq. in. pressure.

In the compressors a peculiar reaction has been noticed when the plant is operating for the manufacture of motor spirit. Contrary to the usual rise of temperature met with when gases are put under pressure, a slight decrease of temperature occurs after compression, caused either by chemical combination or by polymerisation of the lighter constituents.

As much as 70 p.c. of the oil used has been obtained as motor spirit by this process. The temperature at the exit of the tubes is 550°–600°C. for motor spirit, the range covering the slightly different working temperatures required for different oils. The temperatures and pressures employed in the production of aromatic hydrocarbons are essentially higher than those found to be most favourable for motor spirit yields, being 750°C. and 105–110 lbs. per sq. in. A large volume of gas of high thermal value (1350 B.Th.U. per cu. ft.) is an unavoidable but valuable by-product of the operation when working for aromatic hydrocarbons, and the spirit contains only very small quantities of non-aromatic compounds unattacked by strong sulphuric acid.

The patents granted for processes of the class described are exceedingly numerous, and are not, except in a few cases, of sufficient commercial importance to demand detailed description, but the results of instructive researches on the subject of 'cracking,' and the commercial developments form the subject of an excellent paper read before the Institution of Petroleum Technologists,[1] reference to which will afford valuable data from a chemical point of view.

The residue furnished on distillation to about 150°C. of the crude product obtained in processes similar to those described is frequently mixed with the oil supply, and thus subjected to a further decomposition, but, in consequence of the valuable solvent properties it possesses (and this especially applies to the heavy residue similar to creosote oil which is yielded by the operations for aromatic products), an increasingly important agent is available for the dilution of viscous petroleum residuums which otherwise would be of little use for oil fuel.

[1] Jour. Inst. Petr. Tech. vol. iii. pp. 36–120.

The Estimation of Aromatic Hydrocarbons in Petroleum.

The insufficiency of the supplies of aromatic hydrocarbons available from coal-tar introduced the urgent necessity of discovering new sources to satisfy the needs which arose during the war.

Among the new sources which hitherto had been neglected petroleum took a prominent place. It is now well known that the production of benzene and toluene by 'cracking' petroleum residues by means of, say, Hall's or Rittman's process, was one of the methods adopted to ease the situation, but the production of aromatic hydrocarbons by this method was wasteful, in that relatively large proportions of the raw material were converted into gas, unsaturated hydrocarbons of low value, and coke. The fraction containing the required aromatic hydrocarbons also consisted of highly unsaturated hydrocarbons, necessitating the removal of the latter by washing with sulphuric acid, the separation of the individual hydrocarbons by fractionation then becoming comparatively simple with ordinary care.

The motor spirit fraction of crude petroleum usually contains an appreciable proportion of naturally-occurring benzene, toluene, and xylene in association with the aliphatic hydrocarbons of the olefinic, paraffin, and naphthenic series.

The estimation of the total aromatic contents of a motor spirit does not present any serious difficulties, the process being one of absorption by fuming sulphuric acid after washing out the unsaturated aliphatic hydrocarbons with 90 p.c. sulphuric acid, with intermediate washings with alkali and water.

A known volume of spirit at laboratory temperature is washed with 90 p.c. sulphuric acid until the residual hydrocarbons remain constant in volume after separation, the acid is separated and the hydrocarbons are washed with alkali, and then with water. A known volume of the spirit freed from unsaturated substances is then shaken with fuming sulphuric acid in excess until the loss in volume is constant. The percentage loss represents sufficiently accurately the aromatic content of the sample.

When the determination of the individual aromatic hydrocarbons is required the matter becomes more complicated. Owing to the occurrence of mixtures of constant boiling-point of the benzene, toluene, and xylene with the associated aliphatic compounds, separation by careful fractionation becomes sufficiently laborious to render this method unsuitable, as the avoidance of presence of benzene in the toluene fraction, for example, becomes almost impossible. A number of attempts to overcome the difficulty have been made without success by the employment of selective organic solvents such as alcohol, acetone, and aniline, and experimental work by several chemists in preparing the nitro-aromatics or sulphonic acids and then regenerating the hydrocarbons in quantitative yields has been equally unsuccessful.

To S. E. Bowrey the credit is due for having brought the solution of the problem within the regions of possibility by a method based upon the research work of Edeleanu. The method, as described in a paper read before the Institution

of Petroleum Technologists (J. Inst. Petr. Tech. 3, 287–305), is founded upon the fact, established by Edeleanu and elaborated into a process, that paraffinoid and naphthenic hydrocarbons may be rendered free from benzenoid hydrocarbons by extraction with liquid sulphur dioxide.

Bowrey states that the extraction of the aromatic hydrocarbons from the aliphatic compounds is much more efficient at low temperatures, and advantage is taken of the refrigerative effect of evaporating the liquid SO_2 by exhausting the apparatus with a water pump, whereby the temperature is quickly reduced to −35°C.

The apparatus consists of a Dewar flask of about one litre capacity, fitted with a thermometer and gas-tight connections to an inverted SO_2 syphon, a vacuum pump, P_1, and a separating funnel. The tube, T, which communicates with the separating funnel, is drawn

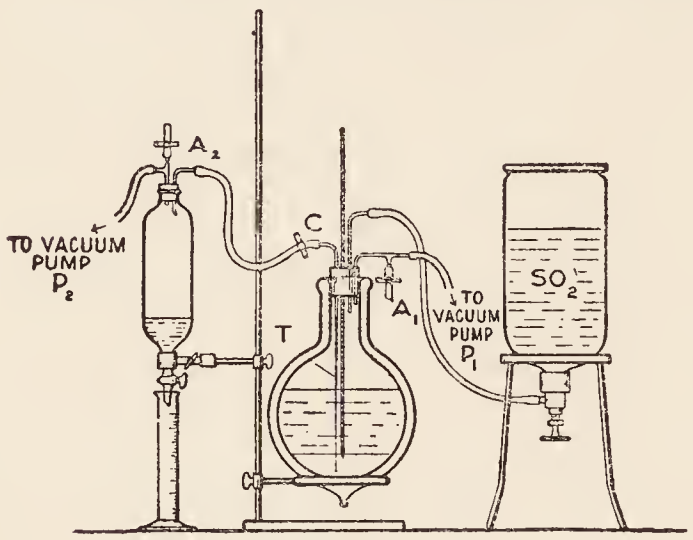


Fig. 38.

out to a capillary, and reaches to the bottom of the Dewar flask. The separating funnel is in turn connected with a second pump, P_2, and both pump connections are provided with air inlets, A_1 and A_2. The SO_2 vapour evolved continues to be drawn into the pumps, even when the vacuum is destroyed by the admission of air, and is dissolved by the water.

500 c.c. of the sample having been placed in the Dewar flask, liquid SO_2 is slowly admitted through the connection, pump P_1 being started with A_1 open.

The temperature in the flask drops quickly to about −8°C., and liquid SO_2 collects in a layer beneath the sample, the sample itself becoming saturated.

Vacuum is now applied by closing A_1, and the liquid SO_2 is thus thrown into ebullition, whereby the contents of the flask are thoroughly agitated together, and the temperature falls to −35°C.

The lower layer of SO_2, with the aromatic hydrocarbons in solution, is now drawn over into the separating funnel (after opening A_1 and screw-clip C) by the action of pump P_2, and C is then closed. The capillary tube permits of clean separation of the two layers.

It is claimed that the low temperature attained eliminates the necessity of cooling the separating funnel beforehand, and, owing to the insulating effect of the frost collecting on the exterior of the funnel, slow evaporation of the SO_2 proceeds without appreciable loss of aromatic hydrocarbons. Bowrey advises the use of a colouring agent in the SO_2 to assist in the separating operation, and suggests a trace of aniline green. When a sufficient number of extractions have been carried out, and a rise of temperature occurs, indicating the completion of the distillation of SO_2, a 10 p.c. solution of caustic solution is admitted to absorb the gaseous SO_2, drawn off again, and the hydrocarbons run out and measured.

A trial mixture having the following volumetric composition :—

Paraffins	85 p.c.
Benzene	5 ,,
Toluene	5 ,,
Xylene	5 ,,

was repeatedly extracted with liquid sulphur dioxide at −35°C.

A table is given, showing in a lucid manner the data obtained.

Ten extractions, each with 10 p.c. by volume of SO_2, gave a total extract of 18·0 p.c. hydrocarbons and a residue of 53·3 p.c. insoluble in SO_2, indicating, by difference, a total evaporation loss of 28·7 p.c. This loss is due to evaporation of pentane and other volatile hydrocarbons, and is quite unimportant so long as it is confined to hydrocarbons other than aromatics.

The extract consisted of 14·16 p.c. of aromatic hydrocarbons and 3·84 p.c. paraffins, as deduced from specific gravities. The residue contained a further 0·27 p.c. of aromatics, as indicated by a nitration test. Hence, 14·43 p.c. out of the 15·0 p.c. taken was accounted for, the loss being 0·57 p.c.

Experiments were conducted which showed that for ordinary work the evaporation losses of the aromatics might reasonably be regarded as consisting of four parts benzene and one part toluene.

For more important work Bowrey gives particulars of refinements in the apparatus which he has introduced to reduce the evaporation losses, the underlying principle being the necessity of keeping the temperature as low as possible throughout the period while the SO_2 is being removed from the extract.

Having obtained by this method a mixture of aromatic hydrocarbons containing aliphatic hydrocarbons as impurity, it becomes essential to resolve the mixture into fractions containing the respective aromatics in order to ascertain the percentages of each.

Owing to the small quantity of extract available and the comparatively large content of aliphatic hydrocarbons, the method of resolution advocated is that of fractionation. Very slow distillation is more important than the type of still-head used, and the difficulty of maintaining a regular and slow distillation prompted the evolution of a self-acting regulator to take the place of adjustment of the gas supply by hand. The design is shown in Fig. 39.

Fractions are cut at 75°, 85°, 105°, 115°, and 130°C., and the specific gravity determined of each. Although, from the nature of the work, the specific gravities of the aliphatic hydrocarbons occurring in the several fractions cannot be obtained with very great accuracy, the specific gravity method affords a rapid and accurate means of making allowance for these hydrocarbons in the aromatics. The

intermediate fractions are sufficiently small in quantity to be considered as mixtures of equal parts of the two aromatic hydrocarbons boiling respectively immediately above and below the range of boiling-points of the fraction, with, of course, the unavoidable quota of aliphatic hydrocarbons without appreciably affecting the accuracy of the result.

For purposes of calculation Bowrey uses the following specific gravities :—

Benzene . . .	0·884 at	$\frac{15·5°C.}{15·5°}$
Toluene . . .	0·870	,,
Xylenes . . .	0·865	,,
Paraffins 75°–85°C. .	0·715	
,, 85°–105° .	0·724	
,, 105°–115° .	0·727	
,, 115°–130° .	0·747	

F. B. Thole has described (J. Soc. Chem. Ind. Trans. 38, 41) a method of estimating benzene and toluene in straight-run petroleum, whereby

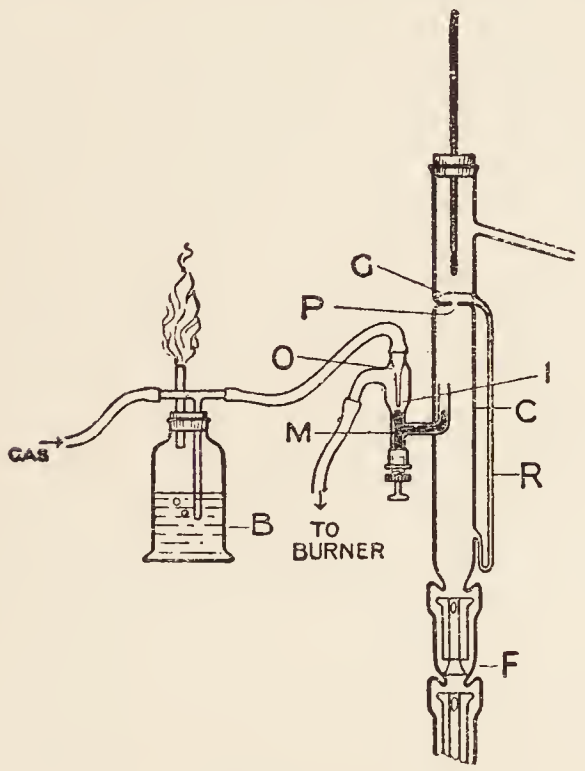


Fig. 39.

the petroleum spirit is distilled to concentrate the aromatic members into separate fractions, each fraction containing all the benzene or toluene as the case may be.

Thole has confirmed the experience of many other chemists, that this is nearly impossible of achievement, because of the tendency to obtain mixtures of constant boiling-point on distillation.

It is suggested that arbitrary cutting temperatures should be selected such that the deficiency of benzene from the benzene fraction shall be balanced by the amount of toluene which distils too soon and is collected in this fraction, and in a similar manner the toluene fraction should be ' cut ' so that the benzene and xylene contained therein are equal in amount to that of the toluene lost in earlier and later fractions. Experimental work has indicated 95°C. and 122°C. as suitable end-points in cutting the benzene and toluene fractions where the amount of aromatics was not large.

The method of treatment of a benzene-petrol or a toluene-petrol has consisted in shaking one volume of the hydrocarbon with three volumes of 98 p.c. sulphuric acid in a stoppered 50 c.c. cylinder. External cooling is only necessary with mixtures rich in aromatic compounds, and the proportion of sulphuric acid is well in excess of requirement with mixtures containing less than 50 p.c. aromatics. With these proportions and a 50 p.c. benzene-petrol, the water resulting from the sulphonation reduces the concentration of the residual sulphuric acid to 96 p.c.; such acid is still capable of effecting sulphonation of benzene. It is advisable to separate the supernatant layer of hydrocarbons when the original sample contains more than half benzene, and treat it with a fresh quantity of acid. For several reasons, the usual procedure of measuring directly the volume of the supernatant layer of unattacked hydrocarbons is liable to larger errors than the alternative method adopted. It is recommended that the specific gravities of the initial fraction and of the residual spirit after acid-washing be determined.

The aromatic component may be calculated to percentage by using the formula :—

$$\frac{\text{Initial specific gravity} - \text{final specific gravity}}{\text{Sp.gr. of aromatic} - \text{final specific gravity}} \times 100$$

The advantages of this method of calculating over direct reading are enumerated as follows : Since specific gravities can be readily determined with precision to the fourth decimal place by means of a 5 c.c. Sprengel pyknometer, a higher degree of accuracy of measurement is attainable, and it is unnecessary to wait for long periods of time until complete separation of the acid and spirit has taken place. Although the sulphonic acids have a solvent action on the non-aromatic hydrocarbons, the final specific gravity is not affected, and hence the calculated aromatic content is not vitiated. If naphthenes are dissolved to a greater extent than paraffins, the error thus introduced is far less than would be found by the ' volume absorption ' method. The specific gravities of aromatics quoted are those due to Perkin (J. Chem. Soc. 1896, 69, 1191) :—

Benzene . .	0·8841 at	$\frac{15·5°C.}{4°}$
Toluene . .	0·8712	,,
o-Xylene . .	0·8807	,,
m-Xylene . .	0·8680	,,
p-Xylene . .	0·8618	,,

It will be seen from the formula that the specific gravity-composition curve for mixtures of aromatic and non-aromatic hydrocarbons is a straight line. Contrary to Bowrey's statement, this is not the case, the specific gravity being slightly lower than that calculated according to the law of mixtures. In other words, expansion in volume takes place when the two classes of hydrocarbons are mixed.

However, by the use of a ' deviation-curve ' this deviation may be corrected for.

The deviation curve does not differ very considerably in the extremes of a paraffinoid and of a naphthenic petrol, and in any case the specific gravity of the non-aromatic hydrocarbons will indicate the nature of these.

Deviation curves have been constructed for the non-aromatic portions of a petrol (40°–95°C.) mainly paraffinoid in nature, and a petrol mainly naphthenic, with benzene, and of the

corresponding fractions of these petrols (95°–122°C.) with toluene.

The non-aromatic portions were prepared by extractions of the fractionated petrols with 98 p.c. sulphuric acid until the specific gravity was constant in each case.

An example will indicate the method of constructing the curve :—

Non-aromatic (95°–122°C.), 11·98 c.c. of sp.gr. 0·7229.
Aromatic, pure toluene, 3·02 c.c. of sp.gr. 0·8712.
Specific gravity of mixture=0·7516.
Volume of mixture

$$=\frac{(11\cdot98\times0\cdot7229)+(3\cdot02\times0\cdot8712)}{0\cdot7516}$$

=15·023 c.c.
Toluene p.c. actually in mixture=20·1 p.c.
Toluene p.c. by sp.gr. method

$$=\frac{0\cdot7516-0\cdot7229}{0\cdot8712-0\cdot7229}\times100=19\cdot35^{\circ}\text{ p.c.}$$

Deviation=0·75 p.c.

The necessary correction to be added to any result drawn from specific gravity determinations can at once be read off from such curves.

Thole makes no allowances for the presence of olefines and sulphur compounds in the petroleum spirit, since these compounds are present to only a small extent in a 'straight-run' petrol, and, although absorbed by the sulphuric acid, do not vitiate the results furnished by the specific-gravity method.

Oil from Shale and Cannel Coal—Testing of Materials.

The production of vast quantities of valuable liquid and solid hydrocarbons from indigenous deposits of shale and cannel coal is a practical possibility. The nature of the products yielded by destructive distillation is largely dependent upon the temperature at which the process of distillation is conducted. An accurate evaluation of the raw material is one of the most important preliminaries of any enterprise in the distillation of shale or cannel coal for commercial products, and can only be ensured by sampling in such a manner that the whole deposit to be worked is truly represented by the sample obtained. Undoubtedly the best method of sampling is that of taking vertical cores of equal section right through the deposit or stratum at regular intervals throughout the length, the whole of the cores being broken to suitable size, and then 'quartered' until the sample is reduced to a less unwieldy bulk. This is crushed to a smaller size and again reduced to a smaller quantity by quartering, the final sample being taken from this by a third quartering operation after the material has been reduced to a fine powder. The crushing of large quantities of material is essentially a laborious task unless the aid of a mechanical crusher is available.

The tests usually required in the first instance are those necessary to indicate the nature and yield of the various products obtainable by retorting the material under working conditions.

The volatile contents, 'fixed carbon,' and ash are estimated by igniting a known weight of the cannel or shale in a crucible, and moisture by drying in a constant-temperature oven under such conditions of temperature and time that the water is expelled without undue oxidation of the sample.

The usual standard methods of estimating volatile matter, 'fixed carbon,' and ash in bituminous materials are applicable, and all results should be obtained by the same method for comparative purposes.

The results furnished by ignition in a crucible are variable to a limited extent according to the method used. A method used for several years has been found to be extremely useful in indicating the yield of oil obtainable—that of igniting 5 grammes of the powdered sample in a porcelain or silica crucible with a closely-fitting lid by a Bunsen burner for one minute after the products of ignition cease to burn at the top of the crucible. The percentage of volatile matter other than moisture may be taken for rough practical purposes as the yield of oil in gallons per ton of material, although for the lower amounts of volatile contents the yield will be somewhat lower than this in practice, whilst for higher values of volatile matter this basis of estimation gives a lower yield of oil than is found in practical working. As stated previously, the yield of oil is very largely dependent on the temperature conditions of retorting, high temperatures being productive of less oil, but more favourable to the formation of ammonia, and the economic question of relative values of these products must largely control the temperature factor. There is a definite relationship between the commercial and technical aspects which has to be borne in mind, and it is therefore essential that determination of the most suitable temperature for economical working should be dealt with. No better preliminary work to this end can be recommended than a series of distillations of the material by means of electrically-heated tube retorts under chemical control, whereby the most favourable temperature for oil production, without an undue proportion of waste gas (waste in the sense that production of gas means loss of oil) may be ascertained, and samples of the oil obtained for subsequent examination of the quality.

The cannel or shale, under the conditions of retorting, loses its volatile constituents and moisture, and these products are led to the condenser, where the liquid and solid portions condense, and the gaseous portion passes to the scrubbers.

The following are obtained as products of the destructive distillation of cannel coal or shale.

(*a*) Water containing some dissolved ammonia.

(*b*) Oil containing paraffin wax.

(*c*) Light oils absorbed in the scrubbers from the gas.

(*d*) Ammoniacal liquor.

(*e*) Coke or ash.

(*f*) Waste gases having an economic value as fuel.

The working-up of these products takes the following course :—

(*a*) is separated from (*b*) and added to (*d*). This liquid is dealt with in accordance with the orthodox gas-works practice for the manufacture of sulphate of ammonia.

The oil (*b*) is allowed to settle at a temperature above the setting-point until suspended water has separated, and is then distilled to about 200°C. to remove the light oils, which are added to the light oils recovered by distillation of the scrubber-oil.

The laboratory work and the procedure to be adopted on the large scale should correspond in general outline. The light oils distilling at 200°C. are distilled to 150°C. in a Wurtz distillation flask, the distillate being motor fuel amounting to about 5 p.c. of the crude oil. The specific gravity at 15·5°C. ranges up to 0·750, and the final boiling-point on redistillation should be about 170°C.

The residue at 150°C. from the redistillation of the light oils should have a minimum flash-point of 73°F. by the Abel test, and not less than 80 p.c. by volume should distil below 200°C. when fractionated by distillation from a Wurtz flask. The demand for such a distillate is increasing rapidly owing to its suitability as a light fuel for tractors. The residue ('bottoms') obtained from the crude oil after removing the light oils will usually possess a setting-point higher than is desired for fuel oils, owing to the presence of solid hydrocarbons, which render the oil solid or semi-solid at ordinary atmospheric temperatures. This feature is more common in the case of cannel oils than with the oil from shales.

For the separation and estimation of the solid paraffin it is necessary to distil the 'bottoms' so that the solid hydrocarbons are obtained in the distillate and the whole of the asphaltic residue remains in the still, the absence of pitch being an essential condition in the separation of the paraffin from the oil. By filtering the cooled distillate, and pressing the soft paraffin between filter-cloths, the percentage of 'paraffin scale' may be determined by weighing the cake from a known quantity of oil. The oil filtrate will now be fluid and suitable for fuel purposes.

The flash-point (close test) of the oil fuel for most applications will be sufficiently high, but in special cases the more volatile portions may have to be removed by 'topping,' so that the flash-point of the residue is not less than 200°F., the 'toppings' being added to the light oils before rectification for motor fuel.

The characteristics of the crude oils which are generally noted are specific gravity, sulphur content, setting-point, water after partial separation, and calorific value. Bases and acids are removed from the various products by acid and alkali treatment.

The pitch residue, which is found to be much more free from fine carbon than the corresponding pitch from bituminous coal-tar, may be dissolved in the intermediate oil to give an oil fuel suitable for use on the works and refinery; tests of such mixtures with varying proportions of the components are of value in indicating the maximum proportion of pitch which may be allocated to this service with due consideration for efficiency and economy.

The sulphur contents of the shale oils are widely different in the case of shales of different origin, and may be as high as 8 p.c. of the oil. A vast amount of experimental work on desulphurisation has been carried out with little promise of immediate success, but the admitted drawback of a large percentage of sulphur may to some extent be overcome by the judicious admixture of crude oils of low and high sulphur contents. B. R.
A. G. V. B.

PETUNIDIN, PETUNIN *v.* ANTHOCYANINS.

PE-TUN-TSE, or **PETUNTZITE** *v.* CHINA-STONE.

PETZITE. Telluride of gold (Au 24–25 p.c.) and silver $(Ag,Au)_2Te$, or Ag_3AuTe_2, since gold and silver are always in the ratio 3 : 1. Crystals have not been found, but the mineral is no doubt isomorphous with the cubic hessite (Ag_2Te). It is iron-black with metallic lustre and a well-marked conchoidal fracture. Sp.gr. 8·7–9·02; H. 2½–3. It usually forms compact, finely granular aggregates, but sometimes the smooth conchoidal fracture may be seen to be continuous over larger areas. The mineral is indistinguishable in appearance from coloradoite (HgTe) with which it often occurs in very intimate association; and it is also very similar to the accompanying fahlerz. It has been found with gold ores in Boulder Co., Colorado, and Calaveras Co., California; and in considerable abundance with other gold tellurides at Kalgoorlie in Western Australia. Occurrences have also been reported from British Columbia and New Zealand. L. J. S.

PEUCEDANUM (ANETHUM) GRAVEOLENS (Benth. et Hook.). The common Dill, cultivated in England and the South of Europe. Has a hot sweetish taste; is used in medicine and for flavouring spirituous cordials.

PEWTER *v.* TIN.

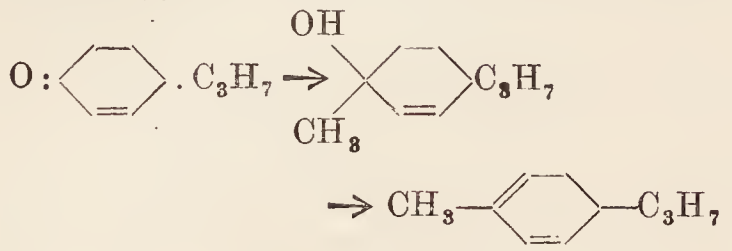
PHASEOLUNATIN *v.* GLUCOSIDES.

PHELLANDRENE $C_{10}H_{16}$ is a terpene which occurs in many oils such as that of *Eucalyptus amygdalina* (Labill.) (Baker and Smith, J. Soc. Chem. Ind. 1899, 302; Wallach, Annalen, 1905, 343, 28); in cinnamon oil (Dayk, Chem. Zentr. 1896, ii. 358; Schimmel & Co., *ibid.* 1910, i. 1720); in the oils of *Schinus molle* (Wallach, *ibid.* 1905, ii. 674); of *Juniperus phœnicea* (Linn.) (Rodié, Bull. Soc. chim. 1906, [iii.] 35, 922); of *Abies sibirica* (Ledeb.) (Schindelmeiser, Chem. Ziit. 1907, 31, 759); of the sassafras bark and leaves (Power and Klebber, Chem. Zentr. 1897, i.e. 42); in the seeds of *Monodoro grandiflora* (Benth.) (Leimbach, *ibid.* 1099, ii. 1870); in elemi oil (Glover, *ibid.* 1907, i. 1794); in the resins of elemi wood (*Canarium luzonicum* [Miq.]) (Wallach and Rheindorf, Annalen, 1892, 271, 310; Bacon, Chem. Zentr. 1909, ii. 1448); in bitter fennel oil (Cahours, Annalen, 1842, 41, 74; Wallach, *ibid.* 1887, 239, 40; *ibid.* 1904, 336, 10); in water fennel oil (*Oenanthe Phellandrium* (Lam.)) from which the name is derived (Pesci, Gazz. chim. ital. 1886, 16, 225), and in many other oils (*see* Biochemisches Handlexikon, 1910, vii. 295).

It is one of the most unstable of the terpenes, and occurs in two modifications, the α- and β- or *pseudo*, the former of which is usually present in greater quantity than the latter. Neither of these has, however, been obtained quite pure (Kondakoff, J. pr. Chem. 1908, [ii.] 78, 42).

α-Phellandrene exists in dextro- and lævo-rotatory modifications. The chief sources of *d*-α-phellandrene are bitter fennel, elemi, and schinus oil. It is also the chief constituent in

the dry distillation of certain elemi resins, whilst the chief source of *l*-α-phellandrene is eucalyptus oil (Wallach, Annalen, 1904, 336, 10). The purest natural α-phellandrene so far obtained had b.p. 61°/11 mm., sp.gr. 0·844 at 19° (*d*—α), and b.p. 65°/12 mm., sp.gr. 0·846 at 19° (*l*—α), at ordinary pressure the b.p. is 173°–176°. The optical rotation depends on the source of the phellandrene. α-Phellandrene has been synthesised from *iso*propyl-Δ²-hexenone by treating the latter with magnesium methyl iodide thus:



(Wallach, Annalen, 1908, 359, 265; *ibid.* 362, 281). It has b.p. 175°–176° (decomp.), sp.gr. 0·841 at 22°.

α-Phellandrene has also been synthesised from Δ⁶-menthene-2-one by treating it with phosphorus pentachloride and reducing the product thus obtained with zinc-dust in methyl alcohol solution, or by reducing menthenone-2-oxime with zinc-dust and glacial acetic acid, and distilling the Δ⁶-mentheneamine so formed *in vacuó* with phosphoric acid. The α-phellandrene so obtained has b.p. 66°/14 mm., 70°/15 mm., sp.gr. 0·8473 at 21° α_D+45° (Harries and Johnson, Ber. 1905, 38, 1832; *see also* Kondakoff and Schindelmeiser, J. pr. Chem. 1905, [ii.] 72, 193; 1907, [ii.] 75, 141).

α-Phellandrene combines directly with two atoms of bromine forming a dibromide which, when boiled with alcoholic potash, yields cymene (Wallach and Herbig, Annalen, 1895, 287, 371; Bacon, *l.c.*). When treated with alcoholic sulphuric acid α-phellandrene yields terpinene (Wallach, Annalen, 1887, 239, 44; 1889, 252, 102); and when reduced with sodium and amyl alcohol it yields dihydrophellandrene (Δ′-*p*-menthene) $C_{10}H_{18}$, b.p. 171°–172°, α_D+25°, sp.gr. 0·829 (Semmler, Ber. 1903, 36, 1035, 1753; Bacon, *l.c.*). On oxidation with potassium permanganate α-hydroxy-β-*iso*propylglutaric acid $C_6H_{14}O_5$ and its lactone $C_8H_{12}O_4$, are formed; but when it is exposed to atmospheric oxygen *dihydroxyphellandrene* $C_{10}H_{18}O_2$ is produced. The latter crystallises in needles, m.p. 164·5°–165·5° (Clover, Amer. Chem. J. 39, 613).

Phellandrene reacts with halogen acids forming mono- and di-additive compounds. *Phellandrene monohydrochloride* has b.p. 80°–83°/1 mm., and when boiled with excess of alcoholic potash yields *dipentene* (Bacon, *l.c.*; *see* also Wallach, Annalen, 1887, 239, 44; Chem. Zentr. 1902, i. 1293; Kondakoff and Schindelmeiser, *l.c.*; Kondakoff, *ibid.* 1908, 78, 42). The most characteristic compounds of phellandrene are the nitrates or nitrosites $C_{10}H_{16}NO{\cdot}NO_2$. They were first discovered by Cahours, and are prepared by the action of nitrogen oxides on the corresponding phellandrene in ligroin solution or by mixing an equal weight of aqueous sodium nitrate with a solution of the phellandrene in light petroleum and then adding gradually the equivalent quantity of glacial acetic acid. They are purified by solution in acetone and fractional precipitation with water or by dissolving in chloroform and precipitating with methyl alcohol (Cahours, *l.c.*; Wallach and Herbig, Annalen, 1895, 287, 373; Wallach, *ibid.* 1900, 313, 345; 1904, 336, 13; Helbronner, Compt. rend. 1901, 133, 43; Schindelmeiser, Chem. Zeit. 1907, 31, 759).

α-Phellandrene yields two modifications which may probably be regarded as *cis*- and *trans*- forms of the nitrosites:—

α-Modification has m.p. 113°–114° (Wallach), 120°–121° (Schreiner, Chem. Zentr. 1901, ii. 544), but according to Clover (*l.c.*) the melting-point depends on the temperature of crystallisation of the nitrosite (*see* also Leimbach, *l.c.*) $[\alpha]_D$+136°–143° (from *l*-phellandrene), $[\alpha]_D$−138° (from *d*-phellandrene).

β-Modification, m.p. 105°–106° $[\alpha]_D$−40·8° (from *l*-phellandrene), $[\alpha]_D$+45·8° (from *d*-phellandrene) (*cf.* Francesconi and Sernagiotto, Gazz. chim. ital. 1916, 46, i. 119).

The nitrosites do not react with bromine, and are not readily attacked by potassium permanganate, the products of oxidation being active *iso*propylsuccinic acid, and *iso*butyric acid. When oxidised with nitric acid, the products are trinitrotetrahydrocymene (chiefly) $C_{10}H_{15}N_3O_6$, m.p. 136°–137°, terephthalic, *iso*-butyric and *iso*propylsuccinic acids. When reduced with zinc-dust and glacial acetic acid, the nitrosites yield *α-phellandrene diamine* $C_{10}H_{16}(NH_2)_2$, b.p. 251°–254°, 132°–134°/17 mm. (Wallach, Annalen, 1902, 324, 270; *ibid.* 1904, 336, 42; Kondakoff, J. pr. Chem. 1903, [ii.] 68, 294), but when reduced with sodium and alcohol, they yield tetrahydrocarveol, and tetrahydrocarvylamine. The action of hydrochloric and of sulphuric acid and of ammonia on the nitrosites has also been studied (Wallach, Annalen, 1904, 336, 26, 28; *ibid.* 1900, 313, 346). When treated in the cold with alcoholic hydrogen chloride β-phellandrene yields α-terpinene hydrochloride (Francesconi and Sernagiotto, Gazz. chim. ital. 1914, 44, ii. 456).

Nitro-α-phellandrene is obtained by the action of alcoholic potash or acetyl chloride on the nitrosite (Annalen, 1887, 239, 42; 1895, 287, 374; 1904, 336, 31; 1900, 313, 349; Semmler, Ber. 1903, 36, 1754). It is a pale yellow oil with a quinone-like odour, b.p. 134°–138°, 125°–129°/9 mm., and gives with sodium and alcohol the same reduction products as the nitrosite. Its optical rotation is in the same sense as that of the nitrosite employed.

β- or *pseudo-Phellandrene* is obtained chiefly from water-fennel oil, also from schinus oil, and in small quantities from that of *Eucalyptus globulus*. Attempts have been made to obtain it synthetically by treating carvomenthenedibromide with alcoholic potash (Kondakoff and Schindelmeiser, J. pr. Chem. 1905, [ii.] 72, 193), or by treating *iso*propylhexenone with bromacetic ester in presence of zinc; then removing water from the hydroxy ester so formed, and hydrolysing the product (Wallach, Chem. Zentr. 1908, i. 2166). The substances so obtained gave the reaction of β-phellandrene, but could not be obtained pure. It has b.p. 170°–172°, 57°/11 mm., sp.gr. 0·8520 at 20°, $[\alpha]_D$+18·54. On reduction it yields the same dihydrophellandrene as the α-compound,

and, like the latter, it combines with two atoms of bromine, forming a dibromide which, unlike the α-dibromide, reacts with alcoholic potash forming a *monobromoethoxy ether*, b.p. 125°–135°/10 mm. (Semmler, Ber. 1903, 36, 1753). β-Phellandrene reacts with hydrochloric acid, forming pinene hydrochloride and dipentene dihydrochloride (Kondakoff and Schindelmeiser, J. pr. Chem. 1907, [ii.] 75, 141).

When β-phellandrene is oxidised with excess of potassium permanganate, the final product is *iso*butyric acid, but at a low temperature and with excess of the hydrocarbon the following products are obtained, 1-*iso*propyl-Δ^2-cyclohexene-4-one, *iso*butyric acid, α-*iso*propylglutaric acid, and a syrupy *glycol* $C_{10}H_{16}(OH)_2$, b.p. 150°/10 mm., which, on distillation with sulphuric acid in steam, gives tetrahydrocuminaldehyde identical with phellandral (Wallach, Annalen, 1905, 340, 1; *see* also Semmler, Ber. 1903, 36, 1749). When oxidised with free oxygen, β-phellandrene yields 1-*iso*propyl-Δ^2-*cyclo*hexene-4-one, b.p. 103°–106°/15 mm., sp.gr. 0·9387 at 26°, the semi-carbazone of which melts at 183°–184° (Wallach, Annalen, 1905, 343, 30).

β-Phellandrene nitrite or *nitrosite* $C_{10}H_{16}N_2O_3$ exists in two modifications; *α-nitrosite* has m.p. 102° $[\alpha]_D$ −159·3°; β-modification has m.p. 97°–98°, and is almost optically inactive (Wallach, Annalen, 1904, 336, 43; 1905, 340, 1).

The nitrates of β-phellandrene are more readily soluble than those of α-phellandrene. On reduction with sodium and alcohol various basic products and cuminaldehyde (m.p. of semi-carbazone, 210°–211°) are formed, whilst if carefully reduced with zinc-dust and acetic acid lævo-rotatory *β-phellandrene diamine*

$$C_{10}H_{16}(NH_2)_2$$

b.p. 260° (decomp.), 133°–135°/11 mm. is formed (Wallach, Annalen, 1902, 324, 278). This diamine gives a number of distinctive derivatives.

Nitro-β-phellandrene $C_{10}H_{15}NO_2$ is obtained by treating the β-nitrosite with ammonia or potash (Pisci, *l.c.*; Wallach, Annalen, 1904, 336, 44; 1905, 340, 3; *ibid.* 343, 38); on reduction it yields dihydrocuminaldehyde, tetrahydrocuminylamine, cuminylamine and other basic substances. According to Bacon (*l.c.*), in addition to the α- and β-phellandrenes, contained in elemi wood resins, there is another phellandrene having b.p. 175°–178°, sp.gr. 0·8375, at 30°/4° $[\alpha]_D^{30°}$ 82·4.

Phellandral (*tetrahydrocuminaldehyde*) (*v. supra*) $C_{10}H_{16}O$ has been obtained from *Phellandrium aquaticum* after removal of the phellandrene, and is contained in certain eucalyptus oils (Penfold, Chem. Soc. Trans. 1922, 121, 266). It is isomeric with citral, and boils at 220°–230°, 89°/5 mm., sp.gr. 0·9445 at 15°, α_D −36° 30′. It gives a semi-carbazone, m.p. 204°, an oxime, m.p. 87°–88°, and a phenylhydrazone, m.p. 122°–123°. On exposure to the air it forms the crystalline acid $C_{10}H_{16}O_2$, and when oxidised with potassium permanganate it yields the dibasic acid $C_9H_{16}O_4$ (J. Soc. Chem. Ind. 1904, 1236).

PHENACETIN (Aceto-*p*-phenetidide)

$$C_2H_5O{\cdot}C_6H_4{\cdot}NH{\cdot}COCH_3$$

is prepared by ethylating *p*-nitrophenol by Kolbe's method (J. pr. Chem. [ii.] 27, 424) reducing the nitrophenetole and acetylating the resulting aminophenetole by boiling with glacial acetic acid (Platt, J. Anal. and Appl. Ch. 1893. 77; Hinsberg, Annalen, 1899, 305, 278; Täuber, D. R. P. 85988).

According to Paul (Zeitsch. angew. Chem. 1896, 587) phenacetin is prepared by heating a mixture of 16·7 grams of *p*-aminophenetole hydrochloride, 8·7 grams of sodium acetate, and 83 grams of acetic acid under a reflux condenser for 3 hours. The mixture is then poured into ten times its volume of boiling water and the solution is filtered. On cooling, phenacetin separates out, and can be purified by repeated recrystallisations. The yield is 90 p.c. of the theoretical.

The successive steps in its commercial production are: (1) nitrating acetanilide; (2) treating the *p*-nitro-compound with alkali to produce the sodium salt of *p*-nitrophenol; (3) converting this by means of ethyl bromide into *p*-nitrophenetole; (4) reducing this to *p*-phenetidine and acetylating the product (J. F. Thorpe).

It crystallises in colourless needles, melts at 135°, and is sparingly soluble in water, soluble in glycerol, and readily soluble in alcohol or acetic acid (Hinsberg and Kast, Chem. Zentr. 1887, 358; Utescher, J. Soc. Chem. Ind. 1888, 87; Seidell, Amer. Chem. J. 1907, 1088). According to Dujardin-Beaumetz (Chem. and Drug. 33, 244), phenacetin, if toxic, is only so in slight degree. It is a safe and trustworthy antipyretic, entirely free from injurious secondary effects, and in doses of 0·2–0·5 gram produces a gradual lowering of temperature during 4–6 hours, when a maximum depression of 2° is reached, D.-B.; H. and K.; U.; Ghillany, J. Soc. Chem. Ind. 1887, 676; Kobler, Chem. Zentr. 1887, 1092; Hoppe, *ibid.* 1888, 609; Rumpf, *ibid.* 188, 1103. In larger doses (1–2 grams) it acts as an anti-neuralgic.

Pure phenacetin should answer to the following tests (Platt, *l.c.*):—

(1) When boiled with hydrochloric acid, the filtrate of the cold diluted solution produces a ruby-red colour on the addition of 2 or 3 drops of potassium dichromate.

(2) After boiling with water, the cooled filtered solution should remain clear on the addition of bromine water.

(3) Boiled with hydrochloric acid and ferric chloride, a red colour is produced.

(4) Boiled with caustic potash, alcohol is produced.

(5) Heated with alcohol and sulphuric acid, ethyl acetate is produced.

(6) Sodium persulphate produces a yellow colour when warmed with phenacetin, and this deepens to orange on boiling.

(7) Bromine water when heated with phenacetin solution gives a rose-colour.

(8) With Millon's reagent phenacetin gives a yellow colour passing to red, nitrous fumes are also given off and a yellow precipitate separates (Barral, J. Pharm. Chim. 1904, 237).

(9) When boiled with phosphoric acid of sp.gr. 1·7 a rose colour is produced, passing through red, violet-bluish-green to a dirty green (Raikow and Schtarbanow, Chem. Zentr. 1900, i. 999).

Phenacetin may contain as impurities or adulterations, acetanilde, antipyrine, quinine, exalgin, and other substances (Mannich, B. Pharm. 1906, 57). It also occurs as an impurity in antipyrine and other pharmaceutical substances. Acetanilide may be detected by the following methods:—

0·1 gram of the sample is boiled with 3 c.c. of a 50 p.c. sodium hydroxide solution, then cooled and shaken with 5 c.c. of sodium hypochlorite solution. If acetanilide be present a purple- or brownish-red turbidity is produced, but if the sample be pure, a clear yellow liquid is obtained (Beringer, Chem. and Drug. 1903, 377).

0·5 gram is boiled with 6 c.c. of water, cooled, filtered, and the filtrate boiled with dilute nitric acid and potassium nitrite. Then a drop or two of Plugge's phenol test is added, and the solution boiled. The appearance of a red colour indicates acetanilide; 2 p.c. of the latter can thus be detected (Schroeder, Arch. Pharm. [iii.] 27, 226). 0·5 p.c. acetanilide can be detected by boiling a gram of the sample with 15 c.c. of water, the solution is then cooled and filtered. On addition of bromine water, a turbidity is produced if the impurity is present owing to the separation of *p*-bromacetanilide (Guasti, L'Orosi, 17, 111).

To detect phenacetin, exalgin, and acetanilide in a mixture, 1 gram of the mixture is treated with 2 c.c. chloroform, which dissolves the exalgin. In aqueous solution antifebrin gives with bromine water a crystalline bromine compound, whereas the other two substances do not give this (Hirschsohn, Pharm. J. 27, 710). Or 2–4 c.c. of the solution is boiled with potash in a test-tube fitted with a rubber cork and bent tube leading into a tube containing 1–3 c.c. of bleaching powder. If acetanilide is present the first few drops produce a violet colour. Exalgin gives a green, turning to a greyish-green colour; if antipyrine is present a yellowish-green colour is produced, whilst if none of these impurities is present, at first the solution remains colourless, then a vermillion-red turbidity is produced, and finally a red substance separates on the surface of the liquid, which itself remains clear yellow (Raikow and Schtarbanow, *l.c.*).

The presence of quinine can be detected by the addition of chlorine water and ammonia when, if quinine is present, a light blue colour will be produced, whereas if the sample is pure the colour is violet-yellow (Sestini and Campani, L'Orosi, 14, 304); or the solution is agitated with bromine vapour and ammonia added drop by drop, the solution turns green, and on being shaken with ether, two layers are formed; the upper is green, indicating quinine, the lower is violet-yellow, and consists of the phenacetin compound (Chem. Zeit. 1893, 368). For other methods and for the detection of other impurities *cf.* Raikow and Schtarbanow, *l.c.*; Luttke, J. Soc. Chem. Ind. 1890, 544; Reuter, Pharm. Zeit. 1891, 185; Goldmann, *ibid.* 208; Platt, *l.c.*; Hyde, Amer. Chem. J. 1895, 933; Schoepp, Pharm. Zeit. 1897, 106; Maas, Chem. Zentr. 1900, ii. 1215. For the estimation of phenacetin *cf.* Turner and Vanderkleed, Pharm. J. 1907, 521; Emery, Spencer and Le Febvre, J. Ind. Eng. Chem. 1915, 5, 681; Analyst, 1915, 40, 445; Salkover, Amer. J. Pharm. 1916, 88, 484; Analyst, 1917, 42, 16; Powell, Analyst, 1919, 44, 22. The last-named author's process affords a convenient method of estimating also other *para*-aminophenol derivatives, and for the analysis of certain photographic developers (rhodinal, metol, 'metol substitutes,' &c.).

When finely-powdered phenacetin is boiled with nitric acid, the solution on cooling deposits silky yellow needles of nitrophenacetin

$$OEtC_6H_3(NO_2)NHAc$$

m.p. 103°. This reaction can serve as a test for distinguishing phenacetin from acetanilide and antipyrine (Autenrieth and Hinsberg, Arch. Pharm. 229, 456). From the nitro-compound *luteol* (*o*-chloro-*m*-hydroxydiphenylquinoxaline), a very sensitive indicator can be prepared (Autenrieth, Chem. Zeit. 1900, 453; Meyer, J. Soc. Chem. Ind. 1909, 328).

With concentrated sulphuric acid phenacetin gives the sulphonic derivative, other compounds being obtained when the strength of the acid is varied (Cohn, Annalen, 1899, 309, 233).

When treated with dry hydrogen iodide phenacetin gives the *hydriodide*

$$(OEt{\cdot}C_6H_4{\cdot}NHAc)_2HI$$

colourless needles, m.p. 147°–148°, and the *hydriododi-iodide* $(C_{10}H_{13}O_2N)_2HI,I_2$ and the *hydriodotetraiodide* (iodophenin)

$$(C_{10}H_{13}O_2N)_2HI,I_4$$

reddish-brown leaflets, or steely-blue prismatic needles, m.p. 133°–134° (Emery, J. Amer. Chem. Soc. 1916, 38, 140). Iodophenin is also formed as a chocolate-coloured crystalline powder by treating a solution of phenacetin in water alcohol, or glacial acetic acid with a solution of iodine in potassium iodide (Riedel, J. Soc. Chem. Ind. 1892, 633; D. R. P. 58409) (*v.* SYNTHETIC DRUGS). *Thiocyanoaceto*-p-*phenetidide*, colourless micro-crystalline powder, m.p. 130°–131° (Beckurts and Frericks, Arch. Pharm. 1915, 253, 233).

Alkylated phenacetins are obtained by treating a solution of phenacetin in xylene solution with sodium and then acting upon the sodium salt thus obtained with the alkyl halide (Willcox, J. Soc. Chem. Ind. 1891, 384); or by treating the acetyl compound of phenacetin with the corresponding alcohol (Willcox, *l.c.* 854).

The *methyl* compound $EtO{\cdot}C_6H_4NMeAc$, m.p. 40°, has more powerful narcotic properties than phenacetin itself, and the *ethyl* compound, m.p. 38°, still more so. The iso-*propyl* and higher alkyl compounds are less powerful narcotics (Hinsberg, Annalen, 1899, 305, 276).

Penacylphenacetin $OEtC_6H_4NAc{\cdot}CH_2COPh$, m.p. 87°, has been prepared in a similar way, and is a non-poisonous hypnotic antipyretic (Goldschmidt, Chem. Zeit. 1901, 628).

By boiling phenacetin (1 mol.) with acetic anhydride (3–4 mols.) a diacetyl derivative is formed, m.p. 53·5°–54°, which has similar physiological properties to phenacetin, its action being more intense but less lasting than the latter (Bistrzycki and Ulffers, Ber. 31, 2788).

Phenacetin has been chlorinated (Reverdin and Düring, Ber. 1899, 32, 152), and brominated (Hinsberg, *l.c.*; Staedel, Annalen, 1883, 217, 73; Vaubel, Ber. 1899, 32, 1875; J. pr. Chem. 1897, [ii.] 217; Hodurek, Ber. 1897, 30, 477).

By the action of chloracetylchloride on *p*-phentidine the chlorine derivative

$$OEt{\cdot}C_6H_4NHCOCH_2Cl$$

m.p. 145°–146°, is obtained (Bistrzycki and Ulffers, *l.c.*).

PHENAKITE or **PHENACITE.** Glucinum orthosilicate Gl_2SiO_4, crystallised in the rhombohedral system with parallel-faced hemihedrism. Analyses correspond closely with the formula (GlO 45·4 p.c.). The crystals are colourless to yellowish, often transparent, and rhombohedral (lenticular) or prismatic in habit. The prismatic crystals may be mistaken for quartz (hence the name, from φέναξ, φένακος, deceiver), but the striations on the faces are here parallel to the prism-edges, whilst in quartz they are perpendicular. Sp.gr. 2·96–3·0; H. = 7½–8; refractive indices (Na) ω = 1·653, ϵ = 1·699. The mineral occurs sporadically in granitic rocks and crystalline schists, but is known from several localities. The best crystals are from the emerald mines near the Takovaya stream in the Ekaterinburg district of the Urals, Kragerö in Norway, and San Miguel de Piracicaba near Ouro Preto in Brazil. It is occasionally used as a gem-stone, and when faceted displays considerable brilliancy.

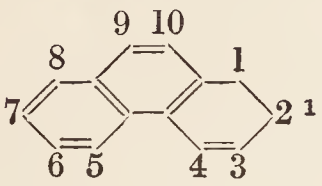
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PHENALGIN. Syn. for phosphoammonio-acetanilide.

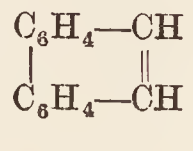
PHENAMINE. Trade name for amino-acet-*p*-phenetidine hydrochloride.

PHENANTHRAQUINONE *v.* PHENANTHRENE.

PHENANTHRENE. 2:2′-*Diphenylene-ethylene*



or



Phenanthrene, isolated from coal-tar almost simultaneously by Fittig and Ostermayer (Ber. 1872, 5, 933; Annalen, 1873, 166, 361), and by Graebe and Glaser (Ber. 1872, 5, 861, 968, 982; Graebe, Annalen, 1873, 167, 131; *cf.* Limpricht, Ber. 1873, 6, 532; Hayduck, Annalen, 1873, 167, 177), is formed together with other hydrocarbons when the vapours of toluene (Graebe, Ber. 1874, 7, 48), stilbene, dibenzyl (Graebe, Annalen, 1873, 167, 157; Barbier, Ann. Chim. Phys. 1876, [v.] 7, 532), turpentine (Schultz, Ber. 1877, 10, 113), or Baku petroleum residues (Letny, Ber. 1878, 11, 1211), or of mixtures of diphenyl and ethylene, benzene and styrene, benzene and ethylene (Barbier, *l.c.*), or cumarone and benzene (Kraemer and Spilker, Ber. 1890, 23, 85) are respectively passed through a red-hot tube. It is also present in the product obtained when morphine or codeïne (Vongerichten and Schrötter, Annalen, 1881, 210, 396; Ber. 1882, 15, 1484, 2179), or morphenol (Vongerichten, Ber. 1898, 31, 3203) is distilled with zinc dust.

Isolation.—For the isolation of phenanthrene the solid portion of crude anthracene readily soluble in crude coal-tar solvent naphtha is used. To ensure freedom from phenols of high boiling-point it is extracted with caustic soda solution and from acridine with sulphuric acid, the residue being then fused with a mixture of sodium and potassium hydroxides to remove carbazole or diphenylene oxide, distilled and that part of the distillate easily soluble in coal-tar naphtha freed from any less soluble impurities still remaining by crystallisation from 95 p.c. alcohol (Clark, J. Ind. Eng. Chem. 1919, 11, 204; *cf.* Schmidt, Ber. 1879, 12, 1159; Wense, Ber. 1886, 19, 761 footnote; Akt. Teer u. Erd-Oel. Ind. D. R.-P. 130679; Eng. P. 5047 of 1901; Kraemer and Weissgerber, Ber. 1901, 34, 1665).

In a mixture of anthracene and phenanthrene, the former is the more easily oxidised. Crude anthraquinone therefore serves as a convenient source of phenanthrene, this hydrocarbon being extracted from it readily by 85 p.c. alcohol (*cf.* Schmidt, J. pr. Chem. 1874, [ii.] 9, 256; Anschütz and Schultz, Annalen, 1879, 196, 35).

On the laboratory scale, phenanthrene is purified conveniently by conversion in alcoholic solution into the *picrate*, which crystallises in golden-yellow needles, m.p. 143°–145°, and on treatment with ammonia yields the pure hydrocarbon (Limpricht, Ber. 1873, 6, 532).

Properties.—Phenanthrene crystallises in monoclinic colourless scales, m.p. 100°, b.p. 340° (Graebe, Annalen, 1873, 167, 131), m.p. 101°, b.p. 332° (Kirby, J. Soc. Chem. Ind. 1921, 40, 274 T). It is insoluble in water, but readily soluble in most organic solvents, showing blue fluorescence in solution. At 16°, 100 pts. of absolute alcohol dissolve 2·62 pts. and at 78°, 10·08 pts. (Bechi, Ber. 1879, 12, 1978); at 13°–14°, 100 pts. of 95 p.c. alcohol dissolve about 2 pts. (Graebe, Annalen, 1873, 167, 136). At 25°, 100 pts. of a saturated solution in absolute alcohol contain 4·91 pts., in benzene 59·5 pts., in carbon disulphide 80·3 pts., in carbon tetrachloride 26·3 pts., in ether 42·9 pts. and in hexane 9·15 pts. (Hildebrand, Ellefson and Beebe, J. Amer. Chem. Soc. 1917, 39, 2301). The solubility in 100 pts. of these and other solvents at 15·5°, 30°, 50°, 80° and 100° has also been determined by Clark, who gives for chloroform and acetone at 15·5° the values 18·7 pts. and 15·08 pts. respectively (J. Ind. Eng. Chem. 1919, 11, 204) and at temperature intervals of 5° between −10° and 30° by Henstock (Chem. Soc. Trans. 1922, 121, 2124).

Reactions.—Oxidising agents usually convert phenanthrene into *phenanthraquinone*, or by further oxidation into *diphenic acid* (Fittig and Ostermayer, *l.c.*), yet with nitric acid it yields not the quinone like anthracene but *nitro*-derivatives like naphthalene. With a large excess of 100 p.c. sulphuric acid and some mercury at 300° *phthalic acid* is obtained (Badische, D. R.-P 91202; Eng. P. 18221 of 1896).

Chlorination in presence of halogen carriers leads to the production of 9 : 10-*dichlorophenanthrene*, needles, m.p. 160°–161° (Schmidt and Ladner, Ber. 1904, 37, 4403), and of 2 : 9 : 10-*trichlorophenanthrene*, needles, m.p. 123°–124° (Schmidt and Schall, Ber. 1906, 39, 3892), but in their absence furnishes either the 9 : 10-*dichloride* mixed with 10-*chlorophenanthrene* or the 9 : 10-*dichloro*-derivative (Sandqvist and Hagelin, Ber. 1918, 51, 1518).

[1] Knorr has proposed that 4 : 5-derivatives should be called *meso*-diderivatives of phenanthrene (Ber. 1903, 36, 3078); also that the numbering of positions in the middle ring should be continued from 10 to 14 (Ber. 907, 40, 3341)

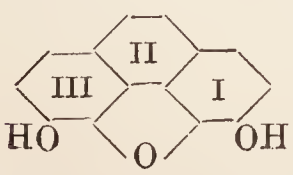
With bromine in the cold it forms the *dibromide*, prisms, m.p. 98°, which, heated at its melting-point, or with water, decomposes into 9 (10)-*bromophenanthrene*, prisms, m.p. 63° (Fittig and Ostermayer, Annalen, 1873, 166, 363; Hayduck, *l.c.*; Zetter,[1] Ber. 1878, 11, 165; Austin, Chem. Soc. Trans. 1908, 93, 1763; *cf.* Sandqvist, Ber. 1915, 48, 1148). Bromination in boiling chloroform solution leads to the formation of 3 : 9- (or 10)-*dibromophenanthrene*, needles, m.p. 146° (Schmidt and Ladner, Ber. 1904, 37, 3577).

Constitution and syntheses.—The structural formula assigned to phenanthrene at the head of this article, adopted originally to exhibit the relationship existing between the hydrocarbon and diphenic acid, its oxidation product, has been confirmed by several syntheses. Of these syntheses, Pschorr's establishes its relationship to ethylene (Ber. 1896, 29, 496), Kenner and Turner's to diphenyl (Chem. Soc. Trans. 1911, 99, 2112), and Ludewig's to naphthalene[2] (Annalen, 1911, 379, 351).

Pschorr's synthetical method (*l.c.*), by which phenanthrene derivatives of known constitution are obtained by the interaction of diazotised α-phenyl-*o*-aminocinnamic acids of appropriate structure with copper powder, has proved to be of wide application, and, coupled with the investigations of Vongerichten and of Knorr, has made it possible for the relationship between phenanthrene and the morphine group of opium alkaloids to be elucidated.

Chemical activity in the phenanthrene molecule is manifested chiefly at the ethylenic double linking, shown between carbon atoms numbered 9 and 10. Here the addition of hydrogen and of bromine takes place, here oxidation leading to the production of phenanthraquinone occurs, and here disruption of the molecule with the formation of diphenic acid follows when more powerful oxidising agents are used. For the purpose of determining orientation in the phenanthrene molecule, oxidation to diphenic acid is important, as—when substituents occur in positions other than 9 or 10 or 9 and 10—they are found in corresponding positions in the resulting diphenic acids.

Phenanthrene has little value in technical chemistry, but its relationship to some of the alkaloids of opium and of *Corydalis* is of much interest. These alkaloids are methoxy- or hydroxy- derivatives of tetra- or hexahydrophenanthrene, the parent substance associated with the nitrogen complex in the case of the opium alkaloids being 3 : 6-dihydroxy-4 : 5-phenanthrylene oxide, in the molecule of which (*a*) rings I and II are hydrogenated in morphine and codeïne, but only ring I in thebaïne; (*b*) the hydroxyl radicle is methylated in ring I in codeïne, but in both rings in thebaïne. Of the *Corydalis* alkaloids bulbocapnine, corytuberine, and corydine



[1] Zetter described two compounds as dibromophenanthrenes, but one of them—the β-compound—is now known to be β-dibromofluorene (Werner and Egger, Ber. 1904, 37, 3027).

[2] Although phenanthrene can be synthesised from naphthalene, the reverse operation has not been accomplished, the lateral rings remaining intact until the middle ring has been broken down by oxidising agents.

less is known, but a relationship has been established between their structure, and that of *apo*morphine (Gadamer, Arch. Pharm. 1911, 249, 503; *cf.* Dobbie and Lauder, Chem. Soc. Trans. 1902, 81, 145).

The connexion between the opium alkaloids and hydroxyphenanthrenes has led to the study of the physiological action of phenanthrene and its derivatives. Phenanthrene and its hydrogenated derivatives are harmless (Hildebrandt, Arch. exp. Path. Pharm. 1908, 59, 140), but 2-, 3- or 9-hydroxyphenanthrene administered subcutaneously gives rise to acute tetanic symptoms, observed also with certain of the carboxylic and sulphonic acids (Bergell and Pschorr, Z. physiol. Chem. 1903, 38, 16). There is no evidence to show that phenanthrene derivatives from the molecules of which a quinoline or *iso*quinoline ring is absent can exercise a narcotic action.

Phenanthrene Hydrides.

9 : 10-*Dihydrophenanthrene* is obtained when phenanthrene is reduced in acetic acid solution containing sodium acetate by adding bromine (1 mol.) in the cold (Henstock, Chem. Soc. Trans. 1921, 119, 1462) or in boiling amyl alcohol solution by sodium, or in presence of finely-divided nickel at 200° by hydrogen (Schmidt and Mezger, Ber. 1907, 40, 4240), or in presence of nickel oxide by hydrogen at 320° under 100 atmos. (Ipatiew, Jakowiew and Rakitkin, Ber. 1908, 41, 999). It forms leaflets from alcohol, m.p. 94°–95°, b.p. 312°–314° under 739 mm., and does not react with bromine. The *picrate* forms scarlet needles, m.p. 135°–137° (Schmidt and Mezger, *l.c.*).

By further reduction α- and β-*tetrahydro*-,[1] and *hexahydro*-, *octahydro*- (*cf.* Tetralin, G.m.b.H. D. R.-P. 333158), *decahydro*- and *dodecahydrophenanthrenes* have been obtained. These compounds are oils, the boiling-point and density of which fall as the amount of hydrogen in the molecule is increased. With the exception of the α-tetrahydro- derivative they do not form picrates (Schmidt and Mezger, *l.c.*).

Phenanthrenesulphonic Acids.

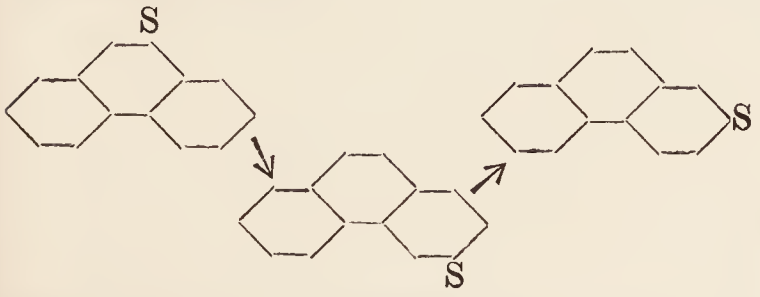
Monosulphonation has been effected by the interaction of phenanthrene with an equal weight of sulphuric acid at 100° (Graebe, Annalen, 1873, 167, 152; Schultz and Japp, Ber. 1877, 10, 1661; Japp, Chem. Soc. Trans. 1880, 37, 83); with two-thirds of this weight at 170°[2] (Morton and Geyer, J. Amer. Chem. Soc. 1880, 2, 203); with an equal weight of sulphuric acid at different temperatures between 80° and 165° (Werner, Annalen, 1902, 321, 257); and with chlorosulphonic acid (Pschorr, Ber. 1901, 34, 4004). Disulphonation has been found to occur when phenanthrene is heated with anhydrosulphuric acid at 100° (Fischer, Ber. 1880, 13, 314).

[1] These tetrahydrophenanthrenes are probably the 2 : 7 : 9 : 10- and 4 : 5 : 9 : 10- derivatives, but it is not known which of them has the former, and which the latter constitution.

[2] The "β-acid" obtained in addition to Graebe's acid by these authors is not identical with Japp's β-acid, and appears to have been the 3-sulphonic acid mixed with some impurity, probably the 2-sulphonic acid (*cf.* Werner, *l.c.*).

Three monosulphonic acids have been shown to occur in the products obtained by the aid of sulphuric acid. The first of these was isolated by Graebe, and converted by Schultz and Japp into a carboxylic acid, oxidisable to phenanthraquinonecarboxylic acid; it is the [α-] or 3-sulphonic acid, as it yields 3-hydroxyphenanthrene on fusion with caustic potash. The second was isolated by Japp, and by him oxidised to phenanthraquinone: it is the [β-] or 9(10)-sulphonic acid. The third is the 2-sulphonic acid discovered by Werner and Rekner (Werner, *l.c.*), which gives 2-hydroxyphenanthrene on fusion with caustic potash. With chlorosulphonic acid the product is a mixture of the 2- and 3-sulphonic acids.

The conditions under which these acids are obtained by means of sulphuric acid is shown in the scheme, which allows a comparison to be made with the course of sulphonation in the naphthalene series:



Best yield at 95°–100°; not detected above 130°. Best yield at 120°–130°; very little above 180°. Good yield at 120°–130°.

For the separation of the isomerides fractional crystallisation of the lead, barium, calcium, or potassium salts is employed, the solubility in water in each case increasing from the 9(10)- to the 2-sulphonic acid (Werner, *l.c.*).

Phenanthrene-2-sulphonic acid has not been crystallised. The *lead* salt, $PbA_2,2H_2O$, is crystalline; the *potassium* salt, KA, and *ammonium* salt, NH_4A, form leaflets; and the *methyl ester* scales, m.p. 96°–98°, which show blue fluorescence (Werner, *l.c.*; Pschorr, *l.c*).

Phenanthrene-3-sulphonic acid forms scales, $HA,2H_2O$, m.p. 88°–89°, HA,H_2O, m.p. 120°–121°; HA, m.p. 175°–177° (Sandqvist, Annalen, 1909, 369, 106). The *lead* salt, $PbA_2,3H_2O$, crystalline granules; *copper* salt, $CuA_2,4H_2O$, scales; *ferrous* salt, $FeA_2,5H_2O$, and *zinc* salt, $ZnA_2,4H_2O$, crystalline powders; *barium* salt, $BaA_2,3H_2O$, scales; *calcium* salt, $CaA_2,2H_2O$, crystalline granules; *magnesium* salt, $MgA_2,4H_2O$, scales; *potassium* salt, KA, scales; *ammonium* salt, NH_4A, scales, have been described (Sandqvist, *l.c.*). The *sulphonyl chloride* crystallises in rhombic prisms, m.p. 110°–111°, also 114°; the *amide* in scales, m.p. 190°; the *methyl ester* in scales, m.p. 119°; and the *ethyl ester* in needles, m.p. 108°.

Phenanthrene-9 (10)-sulphonic acid forms needles; the *barium* salt, $BaA_2,2\frac{1}{2}H_2O$, needles; the *potassium* salt, KA, needles; the *sulphonyl chloride* needles, m.p. 125·5°; and the *anilide* prisms, m.p. 165° (Werner, *l.c.*). For other salts, *cf.* Sandqvist, Annalen, 1912, 392, 76.

Nitrophenanthrenes.

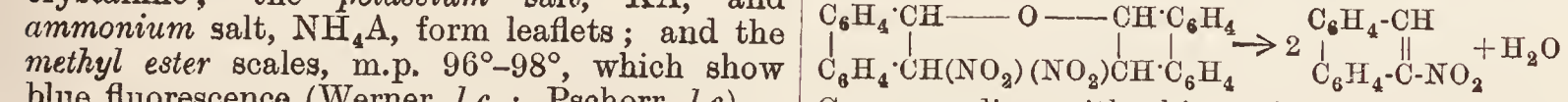
Of the five nitrophenanthrenes only the 1-isomeride remains to be prepared (Schmidt and Heinle, Ber. 1911, 44, 1490).

Earlier work on the nitration of phenanthrene with a large excess of fuming nitric acid led to the isolation of three compounds, termed α- (m.p. 73°–75°), β- (m.p. 126°–127), and γ- (m.p. 170°–171°) nitrophenanthrenes (Schmidt, Ber. 1879, 12, 1153). It has been shown that of these compounds the α- and γ- are identical respectively with 4- and 3-nitrophenanthrenes, whereas the β-compound is a nitro- derivative not of phenanthrene, but of fluorene, which accompanies this hydrocarbon in coal-tar (Schmidt and Heinle, *l.c.*).

For the production of *nitrophenanthrenes* Schmidt has employed two methods. In one, nitration is effected by nitric acid (sp.gr. 1·45) in presence of a mixture of acetic acid and acetic anhydride, leading to the formation of the four isomerides. A summary of the properties and yields of these substances, as recorded by Schmidt and Heinle, is given in the table—

NO_2	Yield (approx.)	Crystallisation from alcohol	M.p.	Picrate
2-	20 p.c.	pale yellow rosettes	99°	none
3-[1]	2 p.c.	deep yellow needles	170°–171°	none
4	20 p.c.	reddish yellow needles	80°–82°	none
9-	60 p.c.	orange yellow needles	116°–117°	98°–99°

In the second method use is made of one of the two additive compounds which phenanthrene, dissolved in benzene, forms with the nitrous gas obtained by the interaction of nitric acid and arsenious oxide. This substance, *nitrodihydrophenanthrene oxide* (m.p. 154°–155°), is converted by sodium methoxide into 9-nitrophenanthrene (Schmidt, Ber. 1900, 33, 3257):



Corresponding with this 9-nitro- derivative, 9-*nitro*-9 : 10-*dihydrophenanthrene*, a yellow crystalline compound, decomposing at 100°, is obtained on mixing phenanthrene in dry powder with the liquefied nitrous gas (Schmidt, D. R.-P. 129990).

Aminophenanthrenes.

Four aminophenanthrenes (phenanthrylamines) are known corresponding in orientation with the nitrophenanthrenes. Three methods have been used for their preparation:—

(i.) Reduction of the nitro- compound by alcoholic ammonium sulphide (Schmidt, Ber. 1879, 12, 1156), *or* stannous chloride and hydrochloric acid (Schmidt and Strobel, Ber. 1901, 34, 1464), *or* zinc-dust and alcoholic ammonia (Schmidt and Heinle, Ber. 1911, 44, 1498).

(ii.) Heating the hydroxy- compound at temperatures above 200° with ammonia (Japp and Findlay, Chem. Soc. Trans. 1897, 71, 1123; Pschorr and Schröter, Ber. 1902, 35, 2728), or ammonio-calcium chloride, or—for the acetyl compound—ammonium chloride, sodium acetate, and acetic acid (Werner and Kunz, Ber. 1901, 3, 2525).

[1] 3-Nitrophenanthrene is obtained in better yield by nitrating phenanthrene with nitric acid of sp.gr. 1·56 at 0° (Schmidt and Heinle, *l.c.*).

(iii.) Conversion of the carboxylic acid successively into hydrazide, azide, and urethane, which is then heated with ammonia (Pschorr and Schröter, *l.c.*; Pschorr, Einbeck, and Spangenberg, Ber. 1907, 40, 2000).

The crystalline character and m.p. of each base and the m.p. of its acetyl and benzoyl derivatives are given in the table—

—	Base	Acetyl	Benzoyl
2-	crystals, 85°	225°–226°	—
3-α-	leaflets, 143°	200°–201°β	213°–214°β
β-	leaflets, 87·5°		
4-	needles, 105°	190°	224°
9-α-	needles, 138°	207°–208°α	190°α
β-	crystals, 104°		

As shown in the table, 3-aminophenanthrene (Werner and Kunz, *l.c.*; Werner, Annalen, 1902, 321, 312; *cf.* Schmidt and Sauer, Ber. 1911, 44, 3247) and 9-aminophenanthrene (Schmidt and Heinle, *l.c.*) exist in two forms—one stable, the other labile and convertible into it by being heated or kept for some time or acetylated. Both forms of each compound give the same acetyl or benzoyl derivative, from which by hydrolysis the stable form of the base (indicated by the Greek letter) is obtained. The nature of the isomerism has not been established, but it has been attributed to rearrangement of the linkings in the phenanthrene molecule in view of the fact that the two forms of the 9-isomeride have the same molecular weight (Schmidt and Heinle, *l.c.*; *cf.*, however, Cadre and Sudborough, Chem. Soc. Trans. 1916, 109, 1349).

Diazotisation of β-3-aminophenanthrene (Schmidt, Ber. 1901, 34, 3534; *cf.* Werner and Kunz, *l.c.*), and of 9-aminophenanthrene [1] (Schmidt and Strobel, Ber. 1903, 36, 2517) has been effected—in the latter case with the accompanying production of azoxy- and azo-compounds. But difficulty has been experienced in diazotising 2-aminophenanthrene (Werner and Kunz, *l.c.*), although 2-amino- (like 8-amino-) phenanthrene-9-carboxylic acid forms a diazo-compound apparently with ease (Pschorr, Ber. 1906, 39, 3121).

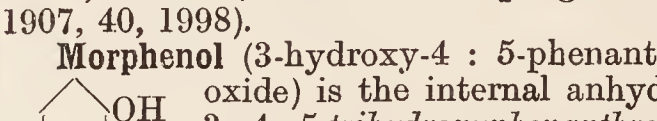
Reduction of phenanthraquinonemonoxime with stannous chloride gives 9 : 10-*amino-hydroxyphenanthrene* and of the dioxime yields 9 : 10-*diaminophenanthrene* (Pschorr, Ber. 1902, 35, 2734; Vahlen, *ibid.* 3044; Schmidt, D. R.-P. 141422). When heated with water or dilute acid, the first of these products is converted into 9-*hydroxyphenanthrene* (Schmidt, *l.c.*).

Hydroxyphenanthrenes.

The hydroxy- derivatives of phenanthrene (phenanthrols) have been investigated largely as a consequence of the relationship which has been established between them, and certain of the opium and *Corydalis* alkaloids. In many cases the constitution of the hydroxyphenanthrenes has been determined by Pschorr's synthetical method, which has shown itself to be of the first importance in the study of the degradation products of these alkaloids. In others, the constitution assigned depends on that of the sulphonic acids, from which some of the hydroxy- derivatives have been obtained by fusion with caustic alkali (*cf.* Werner, Annalen, 1902, 321, 276). The constitution, crystalline character and melting-point of the hydroxyphenanthrenes and of their ethers are given in the table on next page.

Among these hydroxyphenanthrenes there are several, about which the information given in the table needs to be supplemented to make clear their properties and relationships.

9- (or 10-) **Hydroxyphenanthrene**, also known as phenanthrone, affords an example of keto-enolic isomerism in the phenanthrene series. It can be obtained from phenanthraquinone by partial reduction with hydriodic acid (Japp and Klingemann, Chem. Soc. Trans. 1893, 63, 770), or from dichlorophenanthrone by reduction with iron and acetic acid (Lachowicz, J. pr. Chem. 1883, [ii.] 28, 168), and is therefore a ketone



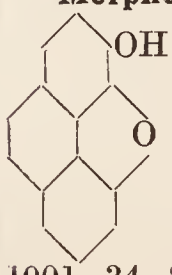
But its formation from phenanthrene-9-sulphonic acid by fusion with caustic alkali, its solubility in alkali, and its conversion into an *ortho*-azo-compound (*phenanthraquinonehydrazone*, m.p. 165°) by coupling with diazotised aniline (Werner and Frey, Annalen, 1902, 321, 298), show it to be phenolic under other conditions.

Hydroxyphenanthrenes from opium alkaloids.

The degradation of opium alkaloids into nitrogen compounds containing relatively few carbon atoms and into derivatives of hydroxyphenanthrene free from nitrogen, has been accomplished by Hofmann's method of exhaustive methylation (Ber. 1881, 14, 494, 663), the products being decomposed by hydrogen chloride (Knorr, Ber. 1894, 27, 1147), acetic anhydride (Fischer and Vongerichten, Ber. 1886, 19, 792), heat (Schrötter and Vongerichten, Ber. 1882, 15, 1485), or hot caustic soda solution (Freund, Ber. 1897, 30, 1379). A list of decomposition products of this type has been given by Knorr and Pschorr (Ber. 1905, 38, 3174).

3 : 4-**Dihydroxyphenanthrene** or **morphol** is formed when acetylmorphine methiodide but its 3-*methyl ether* when acetylcodeïne methiodide is heated with acetic anhydride (Fischer and Vongerichten, Ber. 1886, 19, 792; Knorr, Ber. 1889, 22, 181, 1113; Vongerichten, Ber. 1896, 29, 65; 1897, 30, 2439), or when morphenol methyl ether is reduced by sodium and alcohol (Vongerichten and Dittmer, Ber. 1906, 39, 1719). By the degradation of *apo*morphine the *dimethyl ether* of *morphol-8-carboxylic acid* has been obtained, convertible into *morphol dimethyl ether* (Pschorr, Jaeckel and Fecht, Ber. 1902, 35, 4392; Pschorr, Einbeck and Spangenberg, Ber. 1907, 40, 1998).

Morphenol (3-hydroxy-4 : 5-phenanthrylene oxide) is the internal anhydride of 3 : 4 : 5-*trihydroxyphenanthrene*, into which it is converted by fusion with caustic alkali (Vongerichten and Dittmer, *l.c.*). It is obtained from β-methylmorphimethine methiodide (Vongerichten, Ber. 1898, 31, 54; 1901, 34, 2722), or from morphine without the



[1] The presence of two forms of the 9-isomeride in the reduction product of 9-nitrophenanthrene was not recognised until later (Schmidt and Heinle, *l.c.*), and there is no information to show whether both forms, or only the α-derivative can be diazotised.

OH in	Hydroxyphenanthrenes and their ethers.	References.
1	Has not been isolated. *Methyl ether*, needles, m.p. 105°–106° ; gives *picrate*, needles, m.p. 153°.	Pschorr, Wolfes and Buckow (Ber. 1900, 33, 162).
2	Forms scales, m.p. 169°, couples with diazotised bases ; gives *acetate*, needles, m.p. 142°–143°, and *benzoate*, leaflets, m.p. 139°–140°. *Methyl ether*, leaflets, m.p. 100°–101° ; gives *picrate*, needles, m.p. 124°. *Ethyl ether*, leaflets, m.p. 112°.	Werner and Kunz (Ber. 1901, 34, 2524); Pschorr and Klein (*ibid.* 4005) ; Werner and Rekner (Annalen, 1902, 321, 305) ; Henstock (Chem. Soc. Trans. 1906, 89, 1528).
3	Forms needles, m.p. 122°–123° ; couples with diazotised bases ; gives *picrate*, m.p. 159°, *acetate*, plates, m.p. 115°–116°, and *benzoate*, needles, m.p. 119°. *Methyl ether*, plates, m.p. 63° ; gives *picrate*, red needles, m.p. 124·5°. *Ethyl ether*, m.p. 46°.	Pschorr, Wolfes and Buckow (*l.c.*) ; Pschorr and Sumuleanu (Ber. 1900, 33, 1821) ; Werner and Kunz (*l.c.*) ; Schmidt (Ber. 1901, 34 3535) ; Pschorr (*ibid.* 4006).
4	Crystalline, m.p. 106°–109° ; gives *acetate*, leaflets, m.p. 58°–59°. *Methyl ether*, leaflets, m.p. 68° ; gives *picrate*, red needles, m.p. 187°–188°.	Pschorr and Jaeckel (Ber. 1900, 33, 1826) ; Ludewig (Annalen, 1911, 379, 361).
9 (10)	**Phenanthrone**, forms large needles, m.p. 152°–153° ; couples with diazotised bases ; gives *picrate*, red needles, m.p. 183°, *acetate*, needles, m.p. 77°, and *benzoate*, needles, m.p. 96°–97°. *Methyl ether*, needles, m.p. 96°–97.	Japp and Findlay (Chem. Soc. Trans. 1897, 71, 1115) ; Werner and Frey (Annalen, 1902, 321, 298) ; Pschorr and Schröter (Ber. 1902, 35, 2728).
2 : 3	Has not been isolated. *Dimethyl ether*, leaflets, m.p. 131° ; gives *picrate*, needles, 127°–128°.	Pschorr and Buckow (Ber. 1900, 33, 1829).
3 : 4	**Morphol**, forms long needles, m.p. 143° ; gives *diacetate*, needles, m.p. 159°. 3-*Methyl ether*, needles, m.p. 65° ; gives *picrate*, red needles, m.p. 150°, and *acetate*, needles, m.p. 131°. 4-*Methyl ether*, oil : gives *acetate*, needles, m.p. 93°–94°. *Dimethyl ether*, leaflets, m.p. 44° ; gives red *picrate*, m.p. 105°–106, and *dibromide*, m.p. 123°.	Fischer and Vongerichten (Ber. 1886, 19, 793) ; Knorr (Ber. 1894, 27, 1148 ; 1904, 37, 3497) ; Pschorr and Sumuleanu (Ber. 1900, 33, 1819, 1823) ; Vongerichten (*ibid.* 352, 1825) ; Knorr and Pschorr (Ber. 1905, 38, 3178) ; Pschorr and Dickhäuser (Annalen, 1910, 373, 81) ; Barger (Chem. Soc. Trans. 1918, 113, 218).
9 : 10	Forms needles, m.p. 146° ; gives *monoacetate*, needles, m.p. 168°–170° ; *diacetate*, flat prisms, m.p. 202° ; and *dibenzoate*, m.p. 230°–231°.	Graebe (Annalen, 1873, 167, 146) ; Japp and Klingemann (Chem. Soc. Trans. 1893, 63, 771) ; Pschorr (Ber. 1902, 35, 2736, 3124) ; Knesch (D. R.-P. 151981).
3 : 4 : 5	Forms scales, m.p. 148°. Its anhydride is **morphenol.** *Trimethyl ether*, m.p. 90° ; gives *picrate*, brown scales or needles, m.p. 167°.	Vongerichten and Dittmer (Ber. 1906, 39, 1720) ; Pschorr and Koch (Annalen, 1912, 391, 54).
3 : 4 : 6	Has not been isolated. 3-*Methyl ether*, oil ; gives *diacetate*, m.p. 162°–163°. 3 : 6-*Dimethyl ether* (**thebaol**), m.p. 94° ; gives *acetate*, m.p. 118°–120°. *Trimethyl ether*, oil ; gives *picrate*, m.p. 109°–110°.	Freund (Ber. 1897, 30, 1389) ; Pschorr, Seydel and Stöhrer (Ber. 1902, 35, 4406) ; Vongerichten (*ibid.* 4411) ; Knorr (Ber. 1904, 37, 3499) ; Pschorr and Rettberg (Annalen, 1910, 373, 66) ; Pschorr (Ber. 1912, 45, 2218).
3 : 4 : 8	Has not been isolated. 8-Methyl ether ; *diacetate*, m.p. 155°–156°. 3 : 4-*Dimethyl ether*, prisms, m.p. 182°–183°. 3 : 8-Dimethyl ether ; *acetate*, needles, m.p. 196°. 4 : 8-*Dimethyl ether* (α-ψ-thebaol), leaflets, m.p. 164°–165° ; gives *acetate*, prisms, m.p. 96°–97°. *Trimethyl ether*, leaflets, m.p. 138° ; gives *picrate*, red needles, m.p. 129°, and *dibromide*, needles, m.p. 139°–140°. 3 : 4-*Dimethyl*-8-*ethyl ether*, leaflets m.p. 100° ; gives *picrate*, red needles, m.p. 119°.	Pschorr (Ber. 1900, 33, 183) ; Pschorr, Einbeck and Spangenberg (Ber. 1907, 40, 2000) ; Pschorr and Busch (*ibid.* 2001) ; Knorr and Hoerlein (*ibid.* 2039) ; Pschorr and Loewen (Annalen, 1910, 373, 73) ; Pschorr and Zeidler (*ibid.* 75) ; Pschorr (Ber. 1912, 45, 2219).
3 : 4 : 9 (or 10)	Has not been isolated. 3-Methyl ether ; *diacetate*, needles, m.p. 202°–204°.	Knorr and Schneider (Ber. 1906, 39, 1420) ; Pschorr, Kuhtz and Roth (*ibid.* 3137).
1 : 3 : 5 : 6	3 : 5 : 6-*Trimethyl ether*, no description given. *Tetramethyl ether*, needles, m.p. 108°–109° ; gives *picrate*, red needles, m.p. 147°–148°.	Pschorr and Rettberg (*l.c.*) ; Pschorr and Knoeffler (Annalen, 1911, 382, 50).

isolation of the morphimethine (Vongerichten, Ber. 1900, 33, 358) ; or from morphenol methyl ether by demethylation with hydriodic acid (Vongerichten, Ber. 1898, 31, 3202). It forms needles, m.p. 145°, gives no coloration in alcoholic solution with ferric chloride, dissolves in caustic soda, giving a yellow solution with blue fluorescence, and does not couple with diazotised bases. On reduction it yields *morphol* (Vongerichten, Ber. 1899, 32, 1522). Its *methyl*

ether forms needles, m.p. 65°; *acetate*, needles, m.p. 140°; and *benzoate*, needles, m.p. 123° (*cf.* Knorr, Ber. 1889, 22, 184; Vongerichten, Ber. 1898, 31, 54; 1900, 33, 358; Schryver and Lees, Chem. Soc. Trans. 1901, 79, 578).

Phenanthrenecarboxylic Acids.

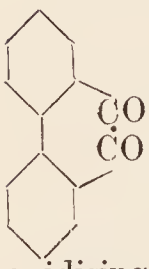
Phenanthrenecarboxylic acids have been prepared by hydrolysis of the nitriles obtained from the three phenanthrenesulphonic acids on distillation with potassium cyanide or ferrocyanide (Schultz and Japp, Ber. 1877, 10, 1661; Japp, Chem. Soc. Trans. 1880, 37, 83; Werner and Kunz, Annalen, 1902, 322, 323). Synthetically Pschorr has obtained the 9-carboxylic acid (Ber. 1896, 29, 496), and the 8 : 9-dicarboxylic acid, the latter of which readily forms a well-crystallised anhydride (m.p. 283°–284°), and exhibits the behaviour of a naphthalene *peri*- derivative (Ber. 1906, 39, 3107).

Phenanthrene-2-carboxylic acid, needles, m.p. 254°; *nitrile*, granules, m.p. 105°; forms *phenanthraquinone-2-carboxylic acid* on oxidation.

Phenanthrene-3-carboxylic acid ([α-] acid), scales, m.p. 269°, forms the *barium* salt, $BaA_2,7H_2O$, sparingly soluble needles; *sodium* salt, $NaA,4H_2O$, easily soluble scales; *amide*, scales, m.p. 227°–228°; *nitrile*, needles, m.p. 102°; and yields *phenanthraquinone-3-carboxylic acid* on oxidation.

Phenanthrene-9-(10-)carboxylic acid ([β-] acid), needles, m.p. 250°–252°, gives the *barium* salt $BaA_2,6H_2O$, sparingly soluble tablets; *sodium* salt, $NaA,5H_2O$, easily soluble rhombic tablets; *amide*, needles, m.p. 226°; *nitrile*, needles, m.p. 103°; and yields *phenanthraquinone* on oxidation.

Dihydrophenanthrene Derivatives.



Phenanthraquinone is a typical member of the series of *ortho*-quinones, but unlike [β-]naphthaquinone, to which it shows a close resemblance in properties, it can be obtained from the corresponding hydrocarbon by direct oxidation. As oxidising agents, use has been made of air at 300°–500° in the presence of oxides of the 5th or 6th group of the Periodic table (Lewis and Gibbs, *cf.* J. Soc. Chem. Ind. 1919, 38, 130A); dichromate mixture (Anschütz and Schultz, Annalen, 1879, 196, 38); chromium trioxide in acetic acid solution (Graebe, Annalen, 1873, 167, 140); sodium chlorate and acetic acid in the presence of ruthenium salts (Badische, D. R.-P. 275518); and electrolytic oxygen in the presence of either manganese sulphate (Lang, D. R.-P. 189178) or cerium sulphate (Meister, Lucius and Brüning, D. R.-P. 152063, Eng. P. 19178 of 1902).

Preparation.—Crude phenanthrene (1 pt.) is stirred in small quantities into a hot solution of sodium dichromate (3 pts.) and concentrated sulphuric acid (9 pts.) in water (15 pts.) and, after the vigorous reaction due to the escape of carbon dioxide has subsided, more dichromate (3 pts.) is added and the mixture heated to the boiling-point for a short time, cooled, diluted with an equal volume of water and filtered. The reddish-yellow, granular product, after being well washed with water, is extracted with warm, concentrated sodium bisulphite solution, in which impurities such as anthraquinone, carbazole, diphenyleneketone, and unattacked hydrocarbons are insoluble, the filtrate poured into dilute sulphuric acid containing some dichromate in solution, and the precipitated phenanthraquinone collected, washed, dried, and crystallised from alcohol (*cf.* Anschütz and Schultz, Annalen, 1879, 196, 38).

Properties.—It crystallises in tufts of long yellow needles, m.p. 205° (Graebe, *l.c.*), boils above 360° without decomposition, sublimes in orange-red prisms, but is odourless and non-volatile with steam. It is only very slightly soluble in water, but dissolves readily in hot alcohol, benzene, or acetic acid. With concentrated sulphuric acid in the cold it gives a green solution, but if benzene containing thiophen be present, the colour is bluish-green, and the liquid, when poured into water and shaken out with ether, gives to the ethereal solution a characteristic reddish-violet coloration, the limit of sensitiveness being reached with 0·0005 gram of the quinone (Laubenheimer, Ber. 1875, 8, 224; Meyer, Ber. 1883, 16, 1624, 2972).

Reactions.—Phenanthraquinone, unlike anthraquinone, dissolves in warm sodium bisulphite solution,[1] being reprecipitated by acids or alkalis. When warmed with sulphurous acid or sulphuretted hydrogen, or phenylhydrazine acetate it is reduced to 9 : 10-*dihydroxy*- (Schmidt and Kämpf, Ber. 1902, 35, 3124), but when boiled with fuming hydriodic acid to 9-*hydroxy-phenanthrene* (Japp and Klingemann, Chem. Soc. Trans. 1893, 63, 770).

With hydroxylamine it forms a *monoxime*, golden-yellow needles, m.p. 158° (Meyer and Auwers, Ber. 1889, 22, 1989), and a *dioxime*, yellow prisms, m.p. 202° (Meyer and Auwers, *l.c.*; Schmidt and Söll, Ber. 1907, 40, 2455), apparently without the production of stereoisomerides. The *anhydride* of the dioxime forms colourless needles, m.p. 186°–187° (Schmidt and Söll, *l.c.*).

Phenylhydrazine in solution converts it into the *hydrazone*, dark red scales, m.p. 162°–163° (Zincke, Ber. 1883, 16, 1564; Werner and Frey, Annalen, 1902, 321, 304), but in the absence of a solvent the product is *phenanthroxazine* (Bamberger and Grob, Ber. 1901, 34, 535).

When boiled with caustic potash solution it is converted into *diphenyleneglycollic acid* (Friedländer, Ber. 1877, 10, 126, 534; *cf.* Schmidt and Bauer, Ber. 1905, 38, 3757), or with caustic alkali solution and permanganate into *diphenyleneketone* (Anschütz and Japp, Ber. 1878, 11, 211), but when boiled with methyl alcoholic potash it gives *diphenic acid* (Meyer and Spengler, Ber. 1905, 38, 443), or with alcoholic potash *diphenic acid* (Anschütz and Schultz, Annalen, 1879, 196, 49) together with an orange-coloured *lactone* $C_{16}H_8O_3$ (Meyer and Spengler, *l.c.*). Distillation with soda-lime furnishes *diphenyl* (Graebe, *l.c.*), but with caustic lime *diphenyleneketone*, *fluorene alcohol*,

[1] The bisulphite compound, $C_{14}H_8O_2,NaHSO_3,2H_2O$ (Graebe, *l.c.*), on reduction in aqueous solution with zinc-dust, also yields 9 : 10-dihydroxyphenanthrene (Knesch, D. R.-P. 151981).

and a small quantity of *fluorene* (Anschütz and Schultz, *l.c.*).

It forms condensation products with many substances, some of which have tinctorial properties although they are of no technical importance as dyestuffs. For example, it has been condensed with arylhydrazinesulphonic acids (Aktienges., D. R.-P. 40745; Eng. P. 6688 of 1887); with mono- alkyl- (or aryl-) *ortho*-diamines (Badische, D. R.-PP. 79570, 90212; Eng. P. 18374 of 1893; 15953 of 1896), or with 1 : 2- or 2 : 3-diaminoanthraquinone (Bayer, D. R.-P. 170562; *cf.* Scholl and Kačer, Ber. 1904, 37, 4532) forming *azines*; with dialkyl-*p*-phenylenediaminethiosulphonic acids forming blue *thiazines* (Fries, D. R.-P. 126963); and with *p*-amino-*m*-hydroxydialkylanilines forming blue *oxazines* (Fries, D. R.-P. 130743). Vat dyes are produced by digesting it or its nitro- derivatives with sulphur (Knoll, D. R.-P. 247186; Badische, D. R.-P. 247415; Eng. P. 18239 of 1911). For other mordant, vat or azine dyes derived from phenanthraquinone, *cf.* Mukherjee and Watson, Eng. P. 9311 of 1915; Chem. Soc. Trans. 1916, 109, 617; Watson and Dutt, *ibid.* 1921, 119, 1211.

Derivatives.—Substitution derivatives of phenanthraquinone are formed either by oxidising phenanthrene derivatives (other than 9-, 10- or 9 : 10- compounds) or by direct substitution, the latter occurring usually in the equivalent 2- and 7- positions which correspond with the *meta*-position in the benzene molecule assumed by the entering radicle under the directing influence of the carbonyl group.

Bromo- derivatives (*cf.* Schmidt, Ber. 1904, 37, 3551). When bromine is added to phenanthraquinone, mixed with sufficient water to form a paste at 0°, a *dibromide* $C_{14}H_8O_2Br_2$ is formed, m.p. 98° (Schmidt and Junghaus, *ibid.* 3556), which, when boiled with water, reverts mainly to the quinone. The minor product of the debromination, 2-*bromophenanthraquinone*, needles, m.p. 233°, is better prepared by brominating the quinone under pressure at 100° (*ibid.* 3358). By further bromination at 150°–160°, 2 : 7-*dibromophenanthraquinone*, needles, m.p. 323°, is obtained (*ibid.* 3567).

Nitro- derivatives (*cf.* Schmidt, Ber. 1903, 36, 3726). Phenanthraquinone, boiled with concentrated nitric acid for 2 minutes, is converted into a mixture of 2-*nitrophenanthraquinone*, golden yellow scales, m.p. 257°–258° (Anschütz and Schultz, Ber. 1876, 9, 1404; Schmidt and Austin, Ber. 1903, 36, 3731), and 4-*nitrophenanthraquinone*, yellow needles, m.p. 179°–180° (Schmidt and Kämpf, *ibid.* 3734). On further nitration the products are 2 : 7-*dinitrophenanthraquinone*, yellow needles, m.p. 300°–303° (Graebe, Annalen, 1873, 167, 144; Schmidt and Kämpf, *l.c.* 3738), and 4 : 5-*dinitrophenanthraquinone*, brownish needles, m.p. 228° (Schmidt and Kämpf, *l.c.* 3745).

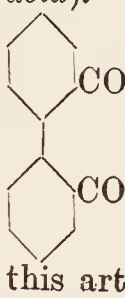
Amino- derivatives. Of these the following have been described: 2-*aminophenanthraquinone*, violet needles, m.p. above 320° (Werner, Annalen, 1902, 321, 338); 3-*aminophenanthraquinone*, dark red needles, m.p. 254° (Werner, *l.c.*; Schmidt and Söll, Ber. 1908, 41, 3694); 2 : 7-*diaminophenanthraquinone*, violet needles, m.p. above 310° (Anschütz and Meyer, Ber. 1885, 18, 1944); and 4 : 5-*diaminophenanthraquinone*, indistinct crystals, m.p. 235° (Schmidt and Kämpf, Ber. 1903, 36, 3750).

Hydroxy- derivatives. The amino- and diamino-phenanthraquinones can be diazotised without difficulty, forming the corresponding *hydroxyphenanthraquinones* (*cf.* Werner, Annalen, 1902, 322, 138, 159; Schmidt and Kämpf, *l.c.*; Schmidt and Leipprand, Ber. 1905, 38, 3733).

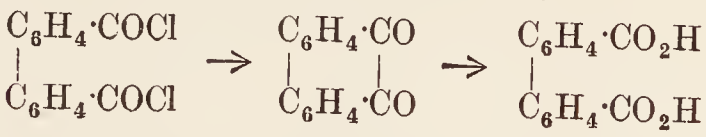
Owing to its relationship to morphine, and the resemblance of some of its properties to those of alizarin, the most interesting of the hydroxyphenanthraquinones is **morpholquinone** (3 : 4-*dihydroxyphenanthraquinone*), which has been obtained from diacetylmorphol by oxidation, followed by diacetylation (Vongerichten, Ber. 1899, 32, 1521), from 3-hydroxyphenanthrene by nitration, reduction, and diazotisation (Schmidt and Söll, Ber. 1908, 41, 3699), and from 3 : 4-dihydroxyphenanthrene by oxidation with silver oxide (Barger, Chem. Soc. Trans. 1918, 113, 220). It forms brilliant red pointed prisms, m.p. 132°–133° (Barger, *l.c.*); gives a *diacetate*, yellow needles, m.p. 196°; and, unlike its isomerides and its monomethyl ether, but like alizarin, forms lakes which with aluminium salts are blue, and with chromium salts deep violet in colour (Vongerichten, *l.c.*).

Diphenyl Derivatives

Diphenic acid (*diphenyl-2 : 2′-dicarboxylic acid*).



From the formula of the hydrocarbon diphenyl, the existence of 15 diphenyldicarboxylic acids can be predicted, but the acids actually known number only about one-third of these, and of them diphenic acid alone requires description in this article. Diphenic acid is closely related to phenanthraquinone; it was first obtained from this substance by oxidation (Fittig and Ostermayer, Annalen, 1873, 166, 367), and its chloride, on reduction with zinc and hydrochloric acid, forms 9 : 10-dihydroxyphenanthraquinone or its oxidation product—phenanthraquinone (Graebe and Aubin, Annalen, 1888, 247, 268)



Preparation.—A solution of phenanthraquinone (1 pt.) in concentrated sulphuric acid (6 pts.) is poured slowly with constant stirring into a solution of sodium dichromate (4 pts.) in water (10 pts.), whereby the quinone is precipitated in a fine state of division. The heat of dilution of the sulphuric acid is sufficient to start the oxidation, and the reaction is completed by boiling the mixture vigorously during 4 hours in a reflux apparatus, the acid being extracted from the precipitate by sodium carbonate solution (Götz, Monatsh. 1902, 23, 27; Graebe and Aubin, *l.c.*; Schmitz, Annalen, 1878, 193, 116). Diphenic acid can also be obtained by boiling phenanthraquinone with aqueous or alcoholic potash (Anschütz and Schultz, Annalen, 1879, 196, 49; Meyer and Spengler, Ber. 1905, 38, 443).

Properties.—It crystallises in scales or monoclinic prisms, m.p. 228°–229° (Schultz, Annalen, 1880, 203, 97), sublimes in needles, is moderately

soluble in hot water, and dissolves readily in alcohol or ether. Dehydrating agents convert it into the *anhydride*; but, when heated with caustic lime, it forms *diphenyleneketone* (*cf.* Schmitz, *l.c.*; Kerp, Ber. 1896, 29, 228), or with slaked lime or soda-lime, *diphenyl* (Anschütz and Schultz, *l.c.*).

Derivatives.—The *barium*, $BaA,4H_2O$, *calcium*, $CaA,2\frac{1}{2}H_2O$, and *magnesium*, $MgA,4H_2O$, salts are crystalline (Fittig and Ostermayer, *l.c.*). The *dimethyl* ester, conveniently prepared from methyl *o*-iodobenzoate and copper powder (Ullmann, Annalen, 1904, 322, 70), forms monoclinic prisms, m.p. 74·5° (Schultz, *l.c.*), and the *diethyl* ester, cubes, m.p. 42° (Hummel, Annalen, 1878, 193, 129). The *chloride* is crystalline, m.p. 93°–94° (Graebe and Aubin, *l.c.*); the *anhydride* forms needles, m.p. 217° (Anschütz, Ber. 1877, 10, 1184; Graebe and Mensching, Ber. 1880, 13, 1302; Graebe and Aubin, *l.c.*); and the *imide*, needles, m.p. 219°–220° (Graebe and Aubin, *l.c.*; Wegerhoff, Annalen, 1889, 252, 16). Certain of its *nitro*-derivatives, contrary to expectation if the nuclei are coplanar, have been resolved into optical isomerides (Christie and Kenner, Chem. Soc. Trans. 1922, 121, 614).

4 : 4′-Diaminodiphenyl-2 : 2′-dicarboxylic acid (m-*diaminodiphenic acid*) is obtained by boiling *m*-hydrazobenzoic acid with concentrated hydrochloric acid (Griess, Ber. 1874, 7, 1069); or, mixed with the 4 : 2′-dicarboxylic acid, by reducing *m*-nitrobenzoic acid with zinc-dust and caustic soda, afterwards extracting the product with hydrochloric acid (Meister, Lucius and Brüning, D. R.-P. 69541); or by reducing 4 : 4′-dinitrodiphenic acid (producible from 2 : 7-dinitrophenanthraquinone by oxidation) with tin and hydrochloric acid (Struve, Ber. 1877, 10, 76; Schultz, *l.c.*).

Properties.—The *acid*, $H_2A,1\frac{1}{2}H_2O$, forms needles, sparingly soluble in water or alcohol, and the *hydrochloride* $H_2A,2HCl$, prisms, sparingly soluble in cold water. When heated with lime it yields *diaminofluorene*, but *benzidine* when the barium salt is heated. The *disazo*-dyes obtained from the *tetrazo*-compound by coupling are not direct cotton dyes, and differ in this respect from those produced by coupling diazotised 4 : 4′-diaminodiphenyl-3 : 3′-dicarboxylic acid (*o*-diaminodiphenic acid) with the same naphthylamine- or naphtholsulphonic acids (Badische, D. R.-PP. 43524, 54662; Eng. P. 9676 of 1890). W. P. W.

PHENANTHRONAPHTHAZINE *v.* AZINES.

PHENANTHROPHENAZINE *v.* AZINES.

PHENAZINE *v.* AZINES.

PHENAZONE. Syn. for antipyrine.

PHENEGEL v. SYNTHETIC DRUGS.

***p*-PHENETIDINE** (*p-aminophenetole*) may be obtained by the action of alcoholic sulphuric, or hydrochloric acid, on phenylhydroxylamine (Bamberger and Lagutt, Ber. 1898, 31, 1560). It may be prepared by adding 212 grams *p*-nitrophenetole gradually to a solution of 848 grams of stannous chloride in 1060 of hydrochloric acid at 50°–60°. It is then precipitated from solution as the hydrochloride by the addition of concentrated hydrochloric acid (Paul, Zeitsch. angew. Chem. 1896, 587).

p-Phenetidine may also be prepared by treating *p*-azophenetole with tin and hydrochloric acid (D. R. P. 48543); or by heating benzylidene-*p*-aminophenol with ethyl bromide and alcoholic sodium hydroxide for 3 hours. The product is then warmed with acid when *p*-phenetidine separates (D. R. P. 69006).

p-Phenetidine is a liquid, b.p. 254·2°–254·7°, m.p. 2·4° (Schneider, Zeitsch. physikal. Chem. 1896, 19, 155). When heated with hydrogen peroxide and dilute sulphuric acid, it yields a brown colouring matter $C_{24}H_{22}N_2O_5$, but when oxidised in the cold with permanganate it yields quinone, carbon dioxide, acetic and oxalic acids, and resinous substances (Kinzel, Arch. Pharm, 229, 329). When to an alcoholic solution, 5 c.c. of a potassium iodide solution are added and the mixture is heated, a rose-red colour is formed (Goldmann, Pharm. Zeit. 1893, 36, 208). For the detection of phenetidine in urine, *see* Edlefsen, Chem. Zentr. 1900, i. 573.

Phenetidine is a stronger febrifuge than phenacetin.

p-Phenetidine sulphonic acid is prepared by heating the hydrogen sulphate of the base or by boiling *p*-nitrophenetole with sodium hydrogen sulphite. It forms readily crystalline sodium salts, and may be diazotised and joined with β-naphthol, thus obtaining the azo- compounds which with barium and aluminium hydroxides form red lakes of great brilliancy and fastness (D. R. P. 146655; *see* also D. R. P. 189469). *p*-Phenetidine sulphonic acid may also be obtained by heating phenetidine with fuming sulphuric acid (Eng. Pat. 14375, 1897; *see* also Cohn, Annalen, 1899, 309, 234; Paul, *l.c.*; Lepetit, Atti R. Accad. Lincei, 1917, [v.] 26, i. 126).

Ethyl sulphone phenetidine

$$EtO\cdot C_6H_4\cdot NHSO_2\cdot C_2H_5$$

is obtained by the action of ethyl sulphochlorides on *p*-phenetidine. It forms shining white leaflets, m.p. 80°–81°, and acts as a monobasic acid, forming well-crystallised salts which may be employed in medicine as they have antineuralgic, antipyretic, sedative and hypnotic properties (Autenrieth and Bernheim, Arch. Pharm. 1904, 242, 579). Similar aromatic sulpho derivatives, also employed in medicine, have been prepared (Eng. Pat. 3791, 1896).

By the interaction of *p*-phenetidine and its homologues with ethyl orthoformate, compounds are formed of the type of methenyldi *p*-phenetidine, which possess anæsthetic properties (Goldschmidt, Chem. Zeit. 1902, 26 743; J. Soc. Chem. Ind. 1890, 650).

The following derivatives of *p*-phenetidine also have medicinal properties:—

The *citrates*, *tartrates*, and *mandelates* prepared by mixing the theoretical quantities of the acid and base dissolved in suitable solvents (Eng. Pat. 11288, 1895).

Lactyl-p-phenetidine (*lactophenin*) is prepared by heating benzylidene *p*-phenetidine with lactic acid (Eng. Pat. 19188, 1894; *see* also Eng. Pat. 29869, 1896). It forms colourless prisms. The *diacetate* of p-*phenetidine*, m.p. 55°–56°, b.p. 182°/12 mm., is obtained by heating phenacetin (p-*phenetidine monoacetate*) with a large excess of acetic anhydride (D. R. P. 75611; Bistrzycki and Ulffers, Ber. 1898, 31, 2788; Cohn, *ibid.* 1899, 32, 2239). *Benzyl*-p-*phenetidine*, m.p. 45°–46°, obtained by heating benzyl chloride with *p*-phenetidine forms crystalline

plates (Wenghöffer, Chem. Zeit. 19, 1753; Wedekind and Fröhlich, Ber. 1907, 40, 1001). *Ethoxyphenyloxamide* $(CO)_2(NH{\cdot}C_6H_4{\cdot}OEt)_2$ by heating anhydrous oxalic acid with *p*-phenetidine to 140°–145°. It forms thin needles, m.p. 263° (Wenghöffer, *l.c.*).

Amygdalyl phenetidine by heating *p*-phenetidine mandelate to 170°, forms shining white plates, m.p. 140·5° (Wenghöffer, *l.c.*). *Ethyl β-phenetidyl crotonate* obtained by condensing *p*-phenetidine with ethyl acetoacetate, forms, when heated rapidly to 225°–240°, p-*ethoxy-γ-hydroxyquinaldine* $EtOC_6H_3{\cdot}NCCH_3{\cdot}C(OH){\cdot}CH$, which has powerful antipyretic properties (Wenghöffer, *l.c.*). *Salicyl*-p-*phenetidene* (*Saliphen*), m.p. 142°–143°, is prepared by heating the constituents with phosphorus oxychloride; its *aceto* derivative has m.p. 92° (U.S. Pats. 706355, 706356, 1902; Bolezzi, Gazz. chim. ital. 1898, 28, ii. 197). Also *amino acet*-p-*phenetidine* (*Phenocoll*), *valeryl*-p-*phenetidine* (*Sedatin*), *vanillin*-p-*phenetidine*, and the *furfural*, *propionyl*, *methyl glycolic*, and *aceto-sulphonic* derivatives (J. Soc. Chem. Ind. 1898, 726; Eng. Pats. 14954, 1896; 4565, 1905).

For the *halogen* derivatives, *see* Staedel (Annalen, 1883, 217, 55); Reverdin (Ber. 1896, 29, 2595); Reverdin and Düring (*ibid.* 1899, 32, 152); Grothe (Arch. Pharm. 1900, 238, 587, 600). Nitro derivatives are described by Wender (Gazz. chim. ital. 19, 218); Autenreith and Hinsberg (Arch. Pharm. 229, 456); Blanksma (Rec. trav. chim. 1905, 24, 40); Lepetit and Maimeri (Atti R. Accad. Lincei, 1917, [v.] 26, i. 559); Hurst and Thorpe (Chem. Soc. Trans. 1915, 107, 938); Reverdin (Arch. Sci. phys. nat. 1912, iv. 34, 330); Reverdin and Fürstenberg (*ibid.* 1913, 35, 594); Dains and Griffin (J. Amer. Chem. Soc. 1913, 35, 959); Van Hove (Bull. Acad. roy. Belg. 1914, 235); Abelin (Annalen, 1916, 411, 229); Reutter (Schweiz. Apoth. Zeit. 1917, 55, 692); Fuchs (Monatsh. 1917, 38, 331); Dains and Harger (J. Amer. Chem. Soc. 1918, 40, 562); Thoms and Nettesheim (Ber. deut. Pharm. Ges. 1920, 30, 227).

For other derivatives, *see* Boettinger (Arch. Pharm. 1896, 234, 158); Wirths (*ibid.* 620); Meves (J. pr. Chem. 1900, [ii.] 61, 449); Vorländer (Annalen, 1897, 294, 273, 302); Bischoff (Ber. 1898, 31, 3241, 3248); Partheil and Schumacher (*ibid.* 591); Sachs and Levy (*ibid.* 1904, 37, 874); Schroeter (*ibid.* 1905, 38, 3181); Bischoff and Fröhlich (*ibid.* 1906, 39, 3976); Erlenmeyer (*ibid.* 791); Goldschmidt (Chem. Zeit. 1901, 25, 178); Lumière and Barbier (Bull. Soc. chim. 1906, [iii.] 35, 123); Fourneau (J. Pharm. Chim. 1910, [vii.] 1, 97).

o-Phenetidine is produced as a by-product in the formation of the para- compound

m-Phenetidine is prepared from *m*-aminophenol by acetylating to *m*-acetylaminophenol, ethylating and hydrolyzing the resulting *m*-acetylaminoethoxybenzene (Reverdin and Lokietek, Bull. Soc. Chim. 1915, 17, 406; 1916, [iv.] 19, 252).

PHENETOLE $C_6H_5{\cdot}O{\cdot}C_2H_5$.

Preparation.—Phenetole can be obtained by heating potassium phenate with ethyl iodide (Cahours, Ann. Chim. Phys. [iii.] 27, 463), or by heating a mixture of equal parts of phenol and phosphorus pentoxide at 200° and gradually adding alcohol (Kastropp, Ber. 1877, 10, 1685). It is prepared by heating molecular proportions of crude calcium or sodium sulphovinate and sodium phenate (prepared by mixing molecular proportions of phenol and aqueous caustic soda of sp.gr. 1·33) at 150° for some hours (Kolbe, J. pr. Chem. [ii.] 27, 424).

It may also be prepared by fusing perfectly dry sodium ethoxide with perfectly dry phenyl sulphonate (Moureu, J. Pharm. Chim. 1898, 8, 211); by the action of sodium ethoxide on triphenyl phosphate (Morel, Compt. rend. 1899, 128, 508); or by passing alcohol into a mixture of phenol and β-naphthalene sulphonate heated to 120°–140° (D. R. P. 76574; Frdl. iv. 18).

Properties.—It is a colourless, aromatic liquid, insoluble in water, but soluble in alcohol or ether. It boils at 172° (Cahours), at 171·5°–172·5° at 762·4 mm. (Schiff, Annalen, 1883, 220, 105), and melts at −33·5°. Combines with mercuric acetate to form $OEt{\cdot}C_6H_5{,}Hg(OH)_2$ (Manchot and Bössenecker, Annalen, 1920, 421, 331).

When phenetole is heated with sulphuric acid or left to stand at ordinary temperatures, p-*phenetole sulphonic* acid, together with a little of the meta-acid separates (Shober and Bowers, Amer. Chem. J. 1901, 25, 69).

Other sulphur compounds of phenetole are described by Gattermann, Ber. 1899, 32, 1136; Taboury, Bull. Soc. chim. 1905, [iii.] 33, 836; Smiles and Rossignol, Chem. Soc. Trans. 1908, 756.

Alkyl phenetoles are obtained by treating a mixture of iodophenetole and ethyl iodide with sodium in benzene solution (Jannasch and Hinrichsen, Ber. 1898, 31, 1824).

Phenetoleazobenzaldehyde sulphonic acid, $C_2H_5O{\cdot}C_6H_4{\cdot}N{:}NC_6H_3(SO_3H)CHO$, is prepared by oxidizing the dye 'Chrysophenin G' with cold aqueous permanganate (Eng. Pat. 1431, 1898). It forms orange-coloured microscopic crystals sparingly soluble in cold, readily in hot water.

By reacting with amino compounds a series of phenetole azo-methineazo dyes have been prepared (Green and Sen, Chem. Soc. Trans. 1910, 2242; v. also AZO- DYES).

Phenetole azo-phenols have been prepared by Jacobson and Meyer (Annalen, 1895, 287, 21); Hewitt, Moore, and Pitt (Ber. 1898, 31, 2114; Chem. Soc. Proc. 1897, 157); *v.* also Naegali (Bull. Soc. chim. 1894, [iii.] 11, 897).

The following derivatives have also been prepared:—

Halogen phenetoles (Autenrieth, Arch. Pharm. 1895, 233, 26; Bentley, Haworth, and Perkin, Chem. Soc. Trans. 1896, 165; Reverdin, Ber. 1896, 29, 2595; Jannasch and Naphtali, Ber. 1898, 31, 1714; Grignard, Compt. rend. 1904, 138, 1048; Autenrieth and Mühlinghaus, Ber. 1906, 39, 4098; Bonneaud, Bull. Soc. Chim. 1910, [iv.] 7, 776; Swarts, Bull. Acad. roy Belg. 1913, 241; Brenans, Compt. rend. 1914, 158, 717).

p-Iodohydroxy phenetole explodes at 225° and has strong oxidising and antiseptic properties (D. R. P. 161725).

Nitro-phenetoles (Lobry de Bruyn, Rec. trav. chim. 13, 101; Blanksma, *ibid.* 1904, 23, 119; *ibid.* 1905, 24, 40; *ibid.* 1908, 27, 49; Paul,

Zeitsch. angew. Chem. 1896, 587; Jacobson and Hönigsberger, Ber. 1903, 36, 4124; Blanksma, Proc. k. Akad. Wetensch. Amsterdam, 1908, 10, 509; Chem. Weekblad, 1908, 5, 789; Marqueyrol and Scohy, Bull. Soc. Chim. 1920, [iv.] 27, 105).

Halogen nitro-phenetoles (Jackson and Calhane, Amer. Chem. J. 1902, 28, 451; Jackson and Gallivan, *ibid.* 1898, 20, 179; Jackson and Fiske, *ibid.* 1903, 30, 53; Jackson and Bigelow, *ibid.* 1911, 46, 549; Jackson and Jones, *ibid.* 1913, 49, 46; Swarts, *l.c.*; Hunter and Joyce, J. Amer. Chem. Soc. 1917, 39, 2640; Reverdin, *l.c.*). *Nitroso phenetoles* (Rising, Ber. 1904, 37, 43).

Phenetole also forms compounds with tellurium chloride and with selenium (Rust, Ber. 1897, 30, 2828; Kunckell, *ibid.* 1895, 28, 609).

For some other derivatives of phenetole *v.* Tust and Gattermann (Ber. 1982, 25, 3528); Pechman and Wedekind (*ibid.* 1895, 28, 1688); Wiechell (Annalen, 1894, 279, 337); Dzierzgowski (J. Russ. Phys. Chem. Soc. 25, 275); Tröger and Volkmer (J. pr. Chem. 1905, [ii.] 71, 236); Tröger and Vasterling (*ibid.* 72, 323); Wfllgerodt and Klinger (J. pr. Chem. 1912, [ii.] 85, 189); Green and Sen (Chem. Soc. Trans. 1912, 101, 1116); M. and R. Robinson (*ibid.* 1917, 934); Rupp and Herrmann (Arch. Pharm. 1916, 254, 488).

p-**PHENETOLECARBAMIDE** *v.* DULCIN.

PHENOCOLL *v.* SYNTHETIC DRUGS.

PHENOCYANINES *v.* OXAZINE COLOURING MATTERS.

PHENOL AND ITS HOMOLOGUES. When a hydroxyl group enters into the molecule of an aromatic hydrocarbon it can do so by replacing (1) a hydrogen atom of the nucleus or (2) a hydrogen atom of a side chain. The isomeric substances thus produced possess, however, very different properties, for, whereas the compound (2) is in all respects analogous to the aliphatic alcohols, the compound (1) exhibits properties which serve to distinguish it entirely from the members of the aliphatic series.

$$\underset{(1)}{C_6H_4(OH)CH_3} \qquad \underset{(2)}{C_6H_5{\cdot}CH_2(OH)}$$

The members of group (1) are therefore classed by themselves, and since the simplest representative of the series, $C_6H_5{\cdot}OH$, which is produced by the substitution of one hydrogen atom of benzene by hydroxyl, is called phenol, all members of the group are known under the general name of phenols.

Nomenclature.—According as one, two, three, four, and so forth, hydroxyl groups enter the benzene nucleus, the phenols are termed monohydric, dihydric, trihydric, tetrahydric phenols respectively. Their scientific names may, in every instance, be referred to the parent hydrocarbon, but in many cases, especially as regards the older members of the series, they are generally known by trivial names which are derived from their mode of origin. Thus 1-3-dihydroxybenzene is termed resorcinol from its similarity to orcinol; 1-2-3-trihydroxybenzene is known as pyrogallol because it was originally prepared by the distillation of gallic acid. The phenols possess the general formula

$$C_nH_{2n-7}(OH) \text{ or } C_nH_{2n-8}O.$$

The Monohydric Phenols. The simplest members of the series frequently occur among the products of the dry distillation of organic compounds containing oxygen, and therefore phenol, and the cresols occur in coal tar. They may be prepared synthetically by the following processes:—

(1) The fusion of a sulphonic acid with potassium hydroxide; thus phenol (potassium salt) is formed from potassium benzene sulphonate in accordance with the equation—

$$C_6H_5{\cdot}SO_3K+2KOH \rightarrow C_6H_5{\cdot}OK+K_2SO_3+H_2O$$

(2) By treating a diazonium salt of an amine with hot water; aniline can be converted into phenol thus—

$$C_6H_5NH_2 \rightarrow C_6H_5N_2Cl+H_2O \rightarrow C_6H_5{\cdot}OH+N_2+HCl$$

The great stability of the halogen derivatives of the aromatic hydrocarbons which have the halogen atoms directly attached to the carbon atoms of the nucleus, prohibits the formation of phenols by the method usually adopted for the preparation of the aliphatic alcohols, namely by the interaction of halogen derivatives of the hydrocarbon and alkaline hydroxides. If, however, a nitro-group is present in the aromatic nucleus, the halogen atom, provided that it is in the ortho- or para-position to the negative group, is readily displaced by hydroxyl thus—

$$C_6H_4(NO_2)Br+KOH \rightarrow C_6H_4(NO_2)OH+KBr$$

A nitro group in the meta- position has no effect on the inactivity of the halogen atom.

(3) Phenols may also be prepared by eliminating the carboxyl group from aromatic hydroxy acids

$$C_6H_4(OH)(CO_2H) \rightarrow C_6H_5(OH)+CO_2$$

General properties.—The phenols differ from the aliphatic alcohols in their capacity for forming salts with alkali metals. The corresponding compounds of the aliphatic alcohols, for example sodium ethoxide, are readily and completely dissociated by water, yielding free alkali and the alcohol

$$C_2H_5{\cdot}ONa+H_2O \rightarrow C_2H_5{\cdot}OH+NaOH$$

whereas a sodium phenolate or phenate $C_2H_5{\cdot}ONa$ dissolves in water without change. The phenols are therefore acid substances which dissolve in aqueous caustic alkalis forming a solution of the salt from which acids reprecipitate the free phenol. The simpler phenols are not, however, acids sufficiently strong to decompose carbonates, but they acquire this property when negative groups are present in the benzene nucleus; thus picric acid dissolves in aqueous alkaline carbonates

$$2C_6H_2(NO_2)_3OH+Na_2CO_3 \rightarrow 2C_6H_2(NO_2)_3ONa+H_2O+CO_2$$

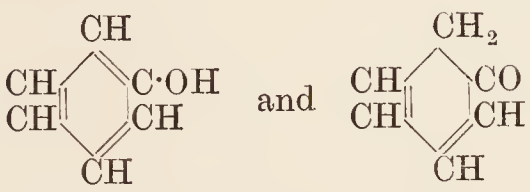
The phenols are therefore weak acids and their alkali salts, which are alkaline to litmus, are readily decomposed by carbonic acid. The action of alkyl iodides on the phenolates yields the phenol ethers, of which anisole, $C_6H_5(OCH_3)$, and phenetole, $C_6H_5(OC_2H_5)$, are types

$$C_6H_5{\cdot}ONa+CH_3I \rightarrow C_6H_5{\cdot}OCH_3+NaI$$

The faintly acid character of phenol is illustrated by the behaviour of these compounds since they are not hydrolysed by alkalis, and are

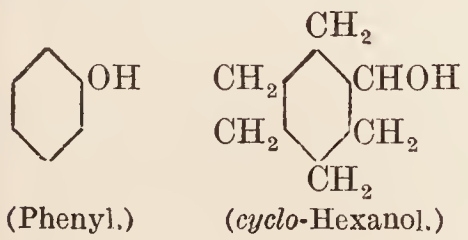
therefore more closely allied in their properties to the ethers than to the ethereal salts. The hydroxyl group in the phenols is readily displaced by hydrogen by distillation with zinc-dust and also by the action of phosphorus trisulphide. It is displaced by halogens through the agency of phosphorus pentabromide or chloride, and by the amino-group by heating with zinc ammonium chloride or similar salts. The replacement of the hydrogen atoms of the nucleus takes place with remarkable readiness, and the entrance of halogen atoms, as well as of nitroso-, nitro-, sulphonic acid, and azo-groups, into the molecule of the phenols can be effected with great ease.

The phenols are characterised by certain colour reactions which may be ascribed to the tendency they possess to react in the tautomeric forms—



Thus well-defined colorations are usually produced by ferric chloride. Other colour reactions are shown by certain reagents; for example, sulphuric acid containing nitrous acid gives a characteristic colour with many phenols; this reaction is the basis of Liebermann's nitroso reaction. Phenols, having free para-positions when fused with phthalic anhydride in the presence of a dehydrating agent, yield phthaleins which dissolve in alkali, forming strongly coloured solutions. The phenols also combine with diazonium salts yielding coloured oxyazo-compounds.

The oxidation of the phenols leads to a variety of products, some produced by the fusion of the aromatic ring, as when phenol is converted into oxalic acid by potassium permanganate (Henriques, Ber. 1888, 21, 1619), but more often leading to derivatives of diphenyl by the joining up of two benzene nuclei. The reduction of the phenols could not be effected until Sabatier and Senderens introduced their process of reduction by the aid of nickel at high temperatures or at 100°–120° under a pressure of 10–15 kilos. per sq. cm. At the present time, practically all the better known phenols have been reduced by this method to the corresponding derivatives of *cyclo*-hexanol. An example may be given in phenol itself which, when its vapour mixed with hydrogen is passed over nickel heated at 215°–230°, is reduced to *cyclo*-hexanol. At the same time, some *cyclo*-hexanone is produced by loss of hydrogen. The mixed product may be either wholly converted into the alcohol by passing it again over nickel at a lower temperature, using a large excess of hydrogen, or into the ketone by conducting the vapour without hydrogen over copper heated at 330° (compare Compt. rend. 1904, 137, 1025; 138, 457, 1257; Brunel, *ibid.* 137, 1268).



(Phenyl.) (*cyclo*-Hexanol.) (*cyclo*-Hexanone.)

Phenol (Carbolic acid, hydroxybenzene). Phenol was discovered by Runge in 1834 (Pogg. Ann. 1834, 31, 69; 32, 308) among the products formed by the distillation of coal tar, and was subsequently obtained in a crystalline condition by Laurent (Annalen, 1842, 43, 200). The preparation of phenol from coal tar is described in the article on carbolic acid (*q.v.*); considerable quantities are made synthetically by the fusion of sodium benzene sulphonate with caustic soda in accordance with the general method already mentioned (1), and the following is a short account of the manufacture. 100 kilos. of benzene and 225 kilos. of sulphuric acid (100 p.c.) are heated together in a jacketed cast-iron pan, the lid of which carries a reflux condenser. The stirrer is kept constantly running and the temperature is maintained at about the boiling-point of benzene. The operation requires about 7–8 hours, when the benzene should be completely sulphonated. The mixture is now run into 300 litres of water and neutralised by adding milk of lime prepared by slaking about 140 kilos. of quick-lime with 700 litres of water. The calcium sulphate is collected in a filter press, washed, and the solution of calcium benzene sulphonate treated with sodium carbonate solution, the calcium carbonate being filtered off and the filtrate evaporated to crystallisation. The crystals are then centrifuged or dried. About 230–235 kilos. of sodium salt (calculated as dry) are obtained.

For the fusion 280 kilos. of sodium benzene sulphonate are added gradually to a mixture of 220 kilos. of caustic soda and 20 litres of water which has been heated in a cast-iron pan to 290°. When the addition is finished the temperature is raised from 290° to 315°–330°, and after 3–4 hours, when the mass is fluid and homogeneous, the latter is run into about 660 litres of water, the sodium sulphite filtered off and the filtrate neutralised with about 190 kilos. of sulphuric acid (50°B.). The phenol rises to the top, and, after the aqueous layer has been drawn off, it is washed with a little water, transferred to a still and distilled, preferably in a vacuum, the first and last runnings being separately collected and put back with the next charge. The yield of phenol from the benzene taken is about 85 p.c. of the theoretical.

Recent patents describe the production of phenol by heating chlorobenzene with caustic soda solution at 300° under very high pressure; The yield is stated to be 90 p.c. (Eng. Pat. 25555 of 1912; U.S. Pat. 1062351; Eng. Pat. 103664; U.S. Pats. 1213142, 1213143); with bromo benzene (Dow, U.S. Pat. 1274394). Calcium benzene sulphonate treated in aqueous solution with sodium sulphate yields calcium sulphate and sodium benzene sulphonate, the latter being fused with caustic soda. The fused mass is dissolved in water and acidified with carbon dioxide and sulphur dioxide derived from a mixture of calcium carbonate and calcium sulphite by the action of sodium hydrogen sulphate, forming calcium sulphate and sodium sulphate and yielding phenol, sodium sulphite and sodium carbonate. These salts treated with lime yield caustic soda and a mixture of calcium sulphite and calcium carbonate, which can be used to produce a further

evolution of carbon dioxide and sulphur dioxide (D. Tyrer, Eng. Pat. 104220). Synthetic phenol has occasionally a repulsive odour which has been attributed to the presence of thiophen in the benzene employed. According to Cappelli (Gazz. chim. ital. 1918, 48, ii. 107) it is caused by the presence of thiophenol formed from particles of sodium benzene sulphonate which during the fusion with alkali escape contact with the latter and undergo deoxidation at the surface of the iron in the manner observed by Stenhouse (Annalen, 1866, 140, 284; 1869, 149, 42). The phenol may be freed from this impurity by fusing it, adding a little alcohol to keep it liquid and then adding per kilo. of phenol about 50 c.c. of 10 p.c. alcoholic mercuric chloride solution and removing the excess of mercuric chloride by copper turnings or foil.

Chlorobenzene heated with an aqueous solution of sodium hydroxide under pressure at 300° yields sodium chloride and sodium phenoxide from which phenol is liberated by acid (Aylsworth, U.S. Pats. 1213142, 1213143).

The cresols fused with caustic soda and copper oxide or the peroxides of lead or manganese and heated at 300° in carbon dioxide yield phenol (Terrisse, Eng. Pat. 108938).

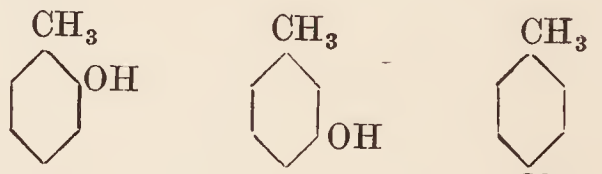
Another improvement in the manufacture of synthetic phenol is the so-called 'liquid fusion,' in which the sodium benzene sulphonate is introduced as a saturated solution into liquid caustic soda at a point above the reaction temperature. For neutralisation of the sodium phenolate the use of carbon dioxide generated from limestone may be used.

Phenol melts at 40·85, boils at 182°/760 mm., or 120·2°/100 mm., and solidifies to a mass of large colourless prismatic crystals possessing a characteristic smell. The presence of 0·2 p.c. of water lowers the m.p. to 40°. With 13·1 p.c. it melts at 8·5°, with 16·7 p.c. at 5°, with 21·9 p.c. at 2·5° (Bennett). The addition of more water causes it to liquefy, since there is formed a solution of water in phenol which is known as 'acidum carbolicum liquefactum.' Phenol forms a definite hydrate $2PhOH,H_2O$, m.p. 15·9°. For a complete freezing-point diagram of the system phenol-water, *see* Rhodes and Markley (J. Phys. Chem. 1921, 25, 527). At the ordinary temperature, about 1 part of water dissolves in 3 parts of phenol. When more water is added an oil separates which ultimately dissolves, yielding a solution of phenol in water; at the ordinary temperature, 1 part of phenol is soluble in 15 parts of water. Phenol is a strong poison, and in its pure condition, or in the form of its concentrated solution, quickly corrodes the skin. It is a powerful aseptic and is employed for this purpose in the form of a 3 p.c. aqueous solution. Phenol is used technically for a variety of purposes; thus it is employed in the preparation of salicylic acid and phenacetin, as well as for the production of picric acid (*q.v.*); it is also the basis of many colouring matters. The presence of phenol (in the absence of other members of the series) may be detected by the violet colour which is produced by ferric chloride, but a more delicate test is to add bromine water to an aqueous solution of the substance, when even in very dilute solution a flocculent pale yellow precipitate of tribromphenol, $C_6H_2Br_3(OH)$, mixed with tribromphenol bromide, $C_6H_2Br_2{\cdot}OBr$, is at once formed.

It may also be identified by giving a characteristic coloured zone when mixed with sodium nitrate solution and poured on the surface of sulphuric acid,

The esters of phenol.—Phenyl hydrogen sulphate, $C_6H_5{\cdot}O{\cdot}SO_2OH$, is formed as the potassium salt when a concentrated solution of potassium phenolate is treated with potassium pyrosulphate. The salt crystallises from alcohol in small glistening leaflets which dissolve in 7 parts of water at 15°. It is stable towards alkalis but is at once decomposed by acids into phenol and acid potassium sulphate. The free acid is unstable both in alcoholic and in aqueous solution. Potassium phenyl sulphate is of some physiological importance since it is in this form that phenol, taken internally, is excreted. It occurs in small quantity in the normal urine of men and dogs. *Phenol methyl ether* (anisole *q.v.*) $C_6H_5{\cdot}OCH_3$, is a pleasant-smelling liquid boiling at 153·9° and melting at −37·8°. It has sp.gr. 0·990 at 22°. *Phenol ethyl ether* (phenetole), $C_6H_5{-}OC_2H_5$, boils at 170·3° and has sp.gr. 0·969 at 16°.

The Cresols. The entrance of a hydroxyl group into the molecule of the hydrocarbon toluene can take place either in the side chain or in the aromatic nucleus. In the former event the compound produced is, as already mentioned, aliphatic in character and need not be considered here. It is only when the hydroxyl group enters the aromatic nucleus that the cresols are formed. It is evident that the hydroxyl group can enter in three positions in respect to the methyl group, and hence there are three cresols which may be represented by the formulæ



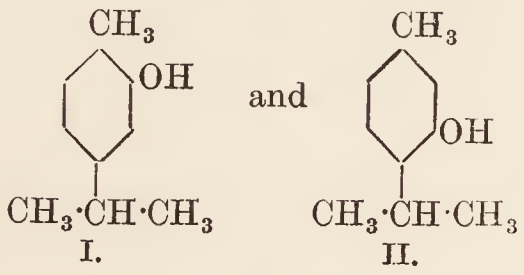
ortho-Cresol. *meta*-Cresol. *para*-Cresol.

All three cresols occur in coal tar in relatively large quantities. Both *o*- and *p*-cresol are prepared in a pure state from the corresponding toluidines through the diazo reaction (method 2). *m*-Cresol is usually derived from thymol by heating it with phosphorus pentoxide. o-*Cresol* (1-methyl-2-hydroxybenzene), melts at 30·60° ±0·02° and boils at 190·8°, conductivity $0{\cdot}127\times10^{-8}$ at 25°. m-*Cresol* (1-methyl-3-hydroxybenzene), melts at 11·10°±0·02°, conductivity $1{\cdot}397\times10^{-8}$ at 25°, and boils at 202·8°. p-*Cresol* (1-methyl-4-hydroxybenzene), melts at 34·55°±0·02, conductivity $1{\cdot}378\times10^{-8}$ at 25°, and boils at 201·8° (*v.* CRESOL).

The six possible *xylenols* (dimethylhydroxybenzenes) have been prepared either from the corresponding xylidines or from the isomeric xylene sulphonic acids by fusion with potash: *adj*-o-*xylenol* (1 : 2-dimethyl-3-hydroxybenzene), melts at 75° and boils at 218°; *asym*-o-*xylenol* (1 : 2-dimethyl-4-hydroxybenzene), melts at 65° and boils at 225°; *adj*-m-*xylenol* (1 : 3 - dimethyl - 2 - hydroxybenzene), melts at 49° and boils at 211°–212°; *asym*-m-*xylenol* (1 : 3-dimethyl-4-hydroxybenzene), melts

at 26° and boils at 11·5°; *sym*-m-*xylenol* (1 : 3-dimethyl-5-hydroxybenzene), melts at 68° and boils at 219·5°; p-*xylenol* (1 : 4-dimethyl-2-hydroxybenzene), melts at 74·5° and boils at 211·5°. The three more important trimethylhydroxybenzenes are: *mesitol* (1 : 3 : 5-trimethyl-2-hydroxybenzene), melting at 70°-71° and boiling at 219·5°; *pseudocumenol* (1 : 2 : 4-trimethyl-5-hydroxybenzene), which melts at 73° and boils at 234°–235°, and *hemimellithenol* (1 : 2 : 3-trimethyl-5-hydroxybenzene), melting at 81°. *Prehnitenol* is 1 : 2 : 3 : 4-tetramethyl-5-hydroxybenzene; it melts at 86°–87° and boils at 266°. *Durenol*, which is 1 : 2 : 4 : 5-tetramethyl-3-hydroxybenzene, melts at 117° and boils at 249°–250°.

Two important substances are included among the higher phenols, namely *carvacrol* and *thymol*. These compounds occur naturally in many ethereal oils and are related to the terpenes and camphors. They are both monohydric phenols derived from cymene (1-methyl-4-*iso*propylbenzene), and since this hydrocarbon can only yield two phenols, namely

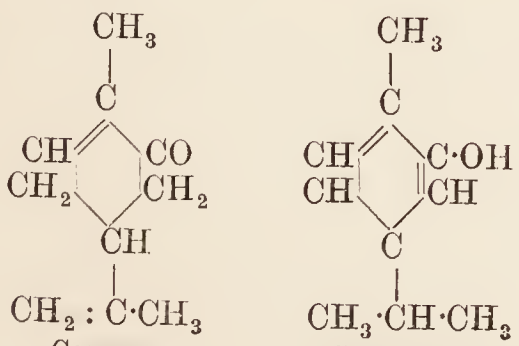


I. II.

it is evident that one must be thymol and the other carvacrol.

The structure of the two compounds is revealed by the fact that when heated with phosphorus pentoxide, cavacrol yields propylene and *o*-cresol; its constitution is therefore represented by formula (I.). Thymol, on the other hand, yields propylene and *m*-cresol under the same conditions and must therefore have the structure represented by formula (II.).

Carvacrol (1-methyl-4-*iso*propyl-2-hydroxybenzene), occurs in the ethereal oils of *Origanum majoranoides* and *Satureja hortensis*, and also in small quantity in the oil of *Thymus serpyllum*. It may be prepared synthetically by fusing sodium cymene sulphonate with caustic soda and can be extracted from the acidified product by means of ether. It is readily formed from its isomeride carvone, a constituent of cumin oil, either by heating with caustic potash or by the action of phosphoric acid. The relation between these substances is shown by the following formulæ—



Carvone. Carvacrol.

It is also derived from camphor by the action of iodine. Carvacrol is a thick liquid which boils at 237° and 95°–96°/5 mm.; it solidifies when cooled and melts at +0·5°. It gives a green coloration with ferric chloride in dilute alcoholic solution.

Thymol (1-methyl-4-*iso*propyl-3-hydroxybenzene) occurs in the essential oils of the common garden thyme, *Thymus vulgaris*; of *Ptychotis ajowan*; and of horsemint, *Monarda punctata*, as well as in the essential oils of *Thymus serpyllium* and *Origanum floribundum* and *O. hirtum*. It may be obtained by shaking oil of thyme with aqueous caustic soda, separating the undissolved terpenes, and acidifying the alkaline extract with hydrochloric acid The precipitated thymol is then recrystallised from acetic acid. It has been synthesised from 3-methoxy-1-methyl-4-ψ-allylbenzene by reducing this with sodium in alcohol to the methyl ether of thymol and demethylating the latter with a mixture of hydrochloric and acetic acids (Béhal and Tiffenean, Bull. Soc. chim. 1908, [iv.] 3, 729).

It may also be prepared by electrolytic reduction of nitrocymene and diazotisation and reduction of the resulting 2-amino-5-hydroxy-1-methyl-4-*iso*propylbenzene (Cole, U.S. Pat. 1378939).

Piperitone, a natural constituent of certain eucalyptus oils when oxidisied with ferric chloride and acetic acid, gives a 25 p.c. yield of thymol (Smith and Penfold, J. Roy. Soc. N.S.W. 1920, 54, 40). Thymol may be obtained by the steam distillation of ajowan seeds, the oil from which amounts to from 2·5–3·5 p.c., containing from 40–45 p.c. of its weight of thymol (Lakhani, Sudborough and Watson, J. Ind. Inst. Sci. 1921, 4, 59).

It may also be prepared by treating sulphonated *m*-cresol with *iso*propyl alcohol and strong sulphuric acid and subsequently splitting off the sulphonyl group (U.S. Pat. 1412937).

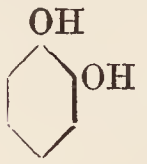
Thymol forms large transparent crystals, soluble in 1100 parts of water at 16°. It is readily volatile with steam, but the aqueous solution is not coloured by ferric chloride. It melts at 50° and boils at 232°. It is a valuable aseptic and can, since it is less poisonous than phenol, be taken internally. When an aqueous solution of thymol is treated with a half part of acetic acid and then with one part of sulphuric acid and warmed, a red-violet colour is produced.

A reaction by which certain higher monohydric phenols can be produced has been introduced by Liebermann (Ber. 1881, 14, 1842). It is carried out by treating aliphatic alcohol, with phenol in the presence of zinc chlorides Thus p-iso*butylphenol* (4-*iso*butyl-1-hydroxybenzene) can be prepared by heating phenol (10 parts), *iso*butyl alcohol (8 parts), and zinc chloride (24 parts) at 180°. It crystallises in needles, melts at 97·4°–98° and boils at 236°–238°. A similar reaction has been discovered by Königs (Ber. 1890, 23, 3145), only in this case the olefinic hydrocarbons are treated with phenol in the presence of a mixture of one part concentrated sulphuric acid and nine parts of glacial acetic acid. The two reactions may be represented by the equations—

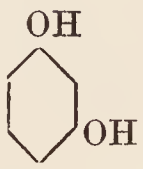
1) $C_4H_9(OH)+C_6H_5\cdot OH \rightarrow C_4H_9\cdot C_6H_4\cdot OH+H_2O$.
(2) $C_5H_{10}+C_6H_5\cdot OH \rightarrow C_5H_{11}\cdot C_6H_4\cdot OH$.

The dihydric phenols. The formula of benzene permits of the existence of three isomeric

dihydroxy derivatives ; their names and formulæ are given below :



1 : 2-Dihydroxybenzene (pyrocatechol).



1 : 3-Dihydroxybenzene (resorcinol).



1 : 4-Dihydroxybenzene (hydroquinone).

As products of the decomposition of naturally occurring substances, these dihydric phenols have been known from the earliest times ; their orientation was first suggested by Petersen (Ber. 1873, 6, 308 ; 1874, 7, 58).

A mixture of the three may be separated by adding lead acetate to their aqueous solution and collecting the lead salt of pyrocatechol. The filtrate is acidified, and the resorcinol and hydroquinone extracted with ether. After evaporating the solution the two phenols are converted into their di-*p*-nitrobenzoates which are separated by crystallisation from acetone (in which the derivative of hydroquinone is very sparingly soluble), and the phenols may be regenerated by hydrolysis (Gray and Cruikshanks, Chem. Soc. Proc. 1914, 30, 305).

Pyrocatechol (1 : 2-dihydroxybenzene) was first obtained by Reinsch in 1839 (Ber. 20, 301) by the dry distillation of catechin (*Mimosa catechu*). It is obtained by the distillation of catechins and is frequently prepared by the distillation of those vegetable substances which give a green coloration with ferric salts (Wagner, Annalen, 1850, 76, 351 ; Uloth, *ibid.* 1859, 111, 215). It is, moreover, formed in the distillation of wood and is therefore present in crude pyroligneous acid.

Preparation.—(1) Pyrocatechol can be made from its methyl ether, *guaiacol*, which is the chief constituent of the fraction of beech wood tar which boils at 200°–205°. The hydrolysis can be effected and a yield of 70 p.c. obtained by the following process (Hartmann and Gattermann, Ber. 1892, 25, 3532). 15 grms. of guaiacol, cooled from without by ice, are gradually mixed with 12 grms. of aluminium chloride and then heated in an oil bath for 2 hours at 210°. At the end of this time the product, which is a hard solid cake, is removed from the flask, ground to powder and warmed with dilute hydrochloric acid, by which process the soluble pyrocatechol is removed from unchanged guaiacol and resinous products. The aqueous extract is then saturated with common salt and the phenol extracted by ether. Pyrocatechol remains on evaporating the solvent and is purified by distillation.

According to Perkin (Chem. Soc. Trans. 1890, 57, 587), an almost quantitative yield of pyrocatechol can be obtained from guaiacol by the following means. A solution of guaiacol in 1·5 times its weight of fuming hydriodic acid (sp.gr. 1·96) is gently heated for about an hour in an apparatus fitted with a reflux condenser (to condense the eliminated methyl iodide), allowed to cool, mixed with a fourth of its weight of hydriodic acid and heated as before for 1 hour. The product, after washing with water, is extracted by ether, the ether removed by distillation and the residual oil purified by rapid fractionation.

(2) Pyrocatechol may be obtained in a pure condition by fusing phenol-*o*-sulphonic acid with 24 molecular proportions of caustic potash at 320°-330° ; the yield is 20 p.c. of the theoretical. By using less potash or a lower temperature a smaller yield is obtained.

(3) It can also be prepared from *o*-chlorophenol by heating it with aqueous alkalis in the presence of copper under pressure to a high temperature (D. R. P. 269544).

Pyrocatechol crystallises from benzene as glistening colourless plates which melt at 104° ; it boils at 240° and is slowly volatile with steam. 31·1 parts are soluble in 100 parts of water at 20°, and the aqueous solution gives a green coloration with ferric chloride, which changes to violet on the addition of sodium carbonate or acetate ; this reaction is characteristic of the ortho-dihydroxy derivatives of benzene. An intense blue coloration is obtained when 2 c.c. of a 0·1 p.c. solution of pyrocatechol are treated with 2 drops of a glycerol extract of *Russula delica* (or other fungus rich in laccase), 5 drops of 3 p.c. potassium iodide solution containing 2 p.c. of soluble starch, and 3 drops of 5 p.c. acetic acid. Hydroquinone gives a similar reaction only when *N*-sulphuric acid is used instead of acetic, and resorcinol gives no reaction under either condition (Wolff, J. Pharm. Chim. 1917, [vii.] 15, 94). The aqueous solution gives a white precipitate with lead acetate, and the formation of this salt, which is insoluble in water, is used for the quantitative estimation of the phenol. The salt can be dried at 100°–110°, and has the composition $C_6H_4O_2Pb$.

Derivatives of pyrocatechol.—The ethers of pyrocatechol are of considerable importance, and many natural products are derivatives of the methyl ethers and especially of the methylene ether (*v.* PIPERONAL).

Guaiacol $OH{\cdot}C_6H_4{\cdot}OCH_3$ was originally prepared by the distillation of guaiacum resin (Unverdorben, Pogg. Ann. 1826, 8, 402), and is also obtained in large quantities by the distillation of wood. It is best derived from the fraction of beechwood tar, boiling at 200°–220° by the following process (Hlasiwetz, Annalen, 1858, 106, 339). The fraction is repeatedly shaken with moderately strong ammonia, then washed with water and rectified. The product is then dissolved in an equal volume of ether, and the potassium salt, which separates on the addition of a slight excess of alcoholic potash, is washed with ether, recrystallised from alcohol, and finally decomposed by dilute sulphuric acid. Guaiacol may be obtained synthetically by direct methylation, for which purpose molecular quantities of pyrocatechol, caustic potash, and potassium methyl sulphate are heated at 170°–180° (Gorup, Annalen, 1868, 147, 248 ; Béhal and Choay, Bull. Soc. chim. 1893, [iii.] 9, 142). It is prepared on the large scale from *o*-anisidine by decomposing the diazo-compound with dilute sulphuric acid heated to 135°–145°, this temperature being obtained by the addition of sodium sulphate ; the guaiacol distils over with the steam as it is formed (Eng. Pat. 7233 of 1897 ; D. R. P. 95339) ; a 50 p.c. solution of copper sulphate may also be used (D. R. P. 167211).

The barium salts of guaiacol and creosol (the

mono-methyl ether of homo-catechol, 3 : 4-dihydroxy-1-methylbenzene) are much less soluble in water than those of the admixed phenols, and a process for the separation of these substances, depending on this property, has been applied technically (D. R. P. 56003, 90). Beechwood tar (40 kilos.) is mixed with barium hydroxide (64 kilos.) and 150 litres of hot water. On cooling, the crystalline magma is filtered off, pressed, washed once with water, and the guaiacol, which is mixed with more or less creosol, separated by the addition of hydrochloric acid and subsequently steam distilled. The distillate, on treatment with aqueous potash, gives the sparingly soluble salts of guaiacol and creosol, the two phenols being finally separated by distillation.

Guaiacol has only within comparatively recent times been obtained in a chemically pure condition (Béhal and Choay, Bull. Soc. chim. 1893, [iii.] 9, 142). It melts at 31°–32° and boils at 205°, dissolves in 60 volumes of water at 15°, and has sp.gr. 1·143 at 15°. A 1 p.c. solution in alcohol gives a blue coloration with ferric chloride, changing quickly through green to yellow. An aqueous solution gives a brown precipitate with 1 or 2 p.c. chromic acid solution and an orange-brown precipitate with iodic acid (Guérin, J. Pharm. Chim. 1903, [vii.] 17, 173). When heated with phosphorus pentachloride it is converted into *o*-chloranisole; a reaction by which its relationship with pyrocatechol and its orientation was originally determined (Fischli, Ber. 1878, 11, 1461).

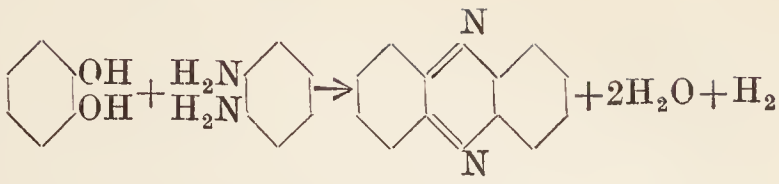
Veratrole $C_6H_4(OCH_3)_2$ (pyrocatechol dimethyl ether, 1 : 2-dimethoxybenzene) is obtained by the distillation of veratric acid with baryta and also by the methylation of the potassium salt of guaiacol (*cf.* Mannich, Arch. Pharm. 1910, 248, 136), or of pyrocatechol (Perkin and Weizmann, Chem. Soc. Trans. 1906, 89, 1649; Tutin, *ibid.* 1910, 97, 2509). It melts at 22·5°, boils at 205°, and has sp.gr. 1·081 at 21·2°.

Other ortho-dihydric phenols. Two methyl derivatives can be derived from pyrocatechol be the entrance of a methyl group into the benzene ring, namely



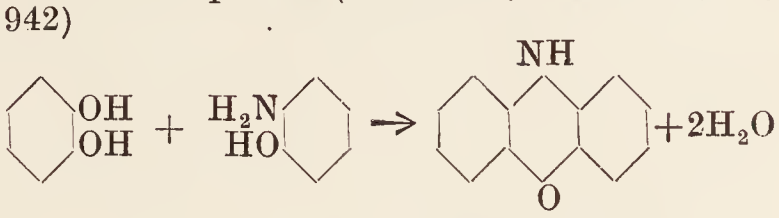
The first is iso*homopyrocatechol*, 2 : 3-dihydroxy-1-methylbenzene, which melts at 47° and boils, with partial decomposition, at 238°–240°. The second is *homopyrocatechol*, 3 : 4-dihydroxy-1-methylbenzene, melting at 65° and boiling at 251°–252°. The methyl ether of this substance, *creosol* (4-hydroxy-3-methoxy-1-methylbenzene), accompanies guaiacol as a constituent of beechwood tar; it melts at 5·5°, boils at 221°–222°, and has sp.gr. 1·111 at 0°.

Reactions of ortho-dihydric phenols.—Apart from the special reactions already mentioned, the ortho-dihydroxy derivatives of benzene are characterised by the following properties. When treated with *o*-phenylenediamine they yield phenazines or derivatives of this substance. Thus pyrocatechol gives phenazine



(Phenazine.)

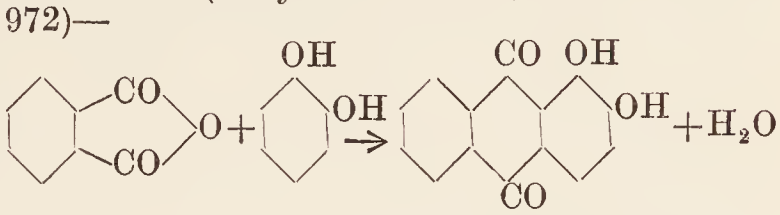
(Ris, Ber. 1886, 19, 2206). With *o*-aminophenols they yield phenoxazines, as is illustrated by the formation of phenoxazine from pyrocatechol and *o*-aminophenol (Bernthsen, *ibid.* 1887, 20, 942)



(Phenoxazine.)

They also yield thiodiphenylamines when treated with *o*-aminothiophenols (Bernthsen, *ibid.* 1887, 19, 3255).

Other typical condensations may be illustrated by the formation of alizarin from phthalic anhydride and pyrocatechol with sulhuric acid (Baeyer and Caro, Ber. 1876, 7, 972)—



(Alizarin.)

and by the production of a phthalein from pyrocatechol and phthalic anhydride in the presence of zinc chloride at 140° (Baeyer and Kochendörfer, Ber. 1889, 22, 2196).

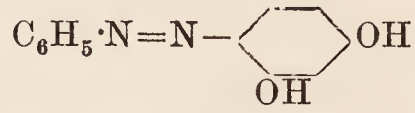
Resorcinol $C_6H_4(OH)_2$ (Resorcin, 1 : 3-dihydroxybenzene) was first obtained by Hlasiwetz and Barth (Annalen, 1864, 130, 354) by melting certain resins (galbanum, &c.) with potash. It is probable that all resins which yield umbelliferone on dry distillation react in this manner (*cf. ibid.* 1866, 139, 83, 100). Resorcinol can also be obtained from benzenedisulphonic acids, halogensulphonic acids and halogenphenols; it is prepared on the technical scale from sodium benzene-*m*-disulphonate by fusion with caustic soda. The preparation from benzene is thus described by Bindschedler and Busch (Mon. Sci. 1878, 1169; J. 1878, 1137). To prepare benzene-*m*-disulphonic acid, 90 kilos. of fuming sulphuric acid are placed in a cast-iron vessel provided with a stirring apparatus, and attached to a reflux condenser, and 24 kilos. of pure benzene are gradually run in with constant stirring; the temperature gradually rises to the boiling-point of benzene, and in the course of two to three hours the benzene is completely converted into the mono-sulphonic acid. The reflux condenser is then removed, the vessel attached to a condenser arranged in the ordinary way, and the temperature raised to 275° in order to convert the mono-sulphonic acid into the disulphonic acid. Any benzene which comes off with the water formed at this stage of the reaction is collected in the receiver. After heating for about 20 minutes at this temperature, the mass is allowed to cool, then poured into 2000 litres of water, neutralised with milk of lime, and converted into the sodium salt in the usual way,

the solution of the salt being subsequently evaporated to dryness. To obtain resorcinol from this product, 60 kilos. of the completely dry sodium salt are added to 150 kilos. of caustic soda dissolved in the smallest possible quantity of water, and the mass heated at 270° in a cast-iron vessel with continual stirring for from 8 to 9 hours, during which time it becomes gradually semi-solid and finally solid. (According to Phillips and Gibbs (J. Ind. Eng. Chem. 1920, 12, 857), the best yields are obtained by using 16 mols. of sodium hydroxide with 1 mol. of sodium benzene-*m*-disulphonate for 2 hours at 310° in presence of not more than 2–4 p.c. of water.) On cooling, it is dissolved in 500 litres of boiling water, the solution acidified with hydrochloric or sulphuric acids and boiled until all sulphur dioxide has escaped. The tarry matter, which is deposited, is filtered off from the cold solution, and the nitrate thoroughly extracted with ether in a copper extraction apparatus, the ether being subsequently distilled off and recovered. The crude resorcinol, obtained in this manner, is a colourless crystalline mass, which can be freed from traces of ether and water by heating it in an enamelled vessel at 215°. It then forms a hard brittle mass containing 92–94 p.c. of resorcinol together with some phenol and about 5 p.c. of tarry matter. To free it from these impurities it is distilled, water coming over first, then phenol and finally resorcinol. It can be further purified by sublimation or recrystallisation from benzene. A similar account of its manufacture is given by Mühlhäuser (Dingl. poly. J. 1887, 263, 154) and by Schoop (Zeitsch. Chem. Ind. 1887, 2, 1), who extract with amyl alcohol instead of with ether. The latter author gives illustrations of the plant required. Resorcinol may also be prepared from *m*-aminophenol through the diazo-compound (Bantlin, Ber. 1878, 11, 2101).

Resorcinol crystallises from benzene in large colourless needles which melt at 110°; it boils at 276·5°, and is slowly volatile with steam: 100 parts of resorcinol dissolve in 67·9 parts of water at 12·5°. It gives a red coloration when heated with nitric acid and the aqueous solution gives a dark violet colour with ferric chloride, which is discharged on the addition of sodium acetate. It gives no precipitate with lead acetate and can, by this means, be distinguished from pyrocatechol. It can be detected in the presence of hydroquinone, pyrogallol, or phenol by the violet colour it gives with cobalt salts (J. Amer. Chem. Soc. 1916, 38, 2182). Resorcinol gives a voluminous precipitate of tribromresorcinol with bromine water and reduces both ammoniacal silver nitrate solution and Fehling's solution when warmed. On fusion with potash it is converted into a mixture of phloroglucinol (60–70 p.c.), pyrocatechol (2–3 p.c.), and diresorcinol (1·5 p.c.) (Barth and Schreder, Ber. 1881, 12, 503).

When fused with phthalic anhydride, resorcinol is converted into fluorescein and the presence of small quantities can be detected by means of this reaction. The test is best effected by dissolving the substance in dilute ammonia and pouring the solution into a large volume of water, when the presence of resorcinol is indicated by the formation of a yellow solution having a fine green fluorescence.

Resorcinol and its analogues (the aminophenols, &c.) are extensively used in the preparation of colouring matters (*see* PYRONINE COLOURING MATTERS). It combines with diazonium salts forming oxyazo colouring matters of which Sudan G is a type



Sudan G.

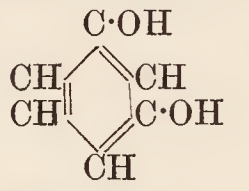
and bisazo- and trisazo- compounds have been prepared, but these compounds have little technical importance.

Resorcinol may be estimated quantitatively by titration with bromine water or by means of a solution of bromine in alkali, as in the case of phenol (*see* Pence, J. Ind. Eng. Chem., 1911, 3, 820). The method is based on the formation of tribromresorcinol in accordance with the equation

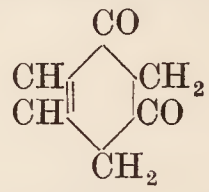
$$C_6H_4(OH)_2+3Br_2 \rightarrow C_6HBr_3(OH)_2+3HBr$$

Delicate tests for resorcinol are described by Carobbio (Chem. Zentr. 1906, [ii.] 632), Silbermann and Ozorovitz (*ibid.* 1908, [ii.] 1022), and by Voley-Boucher and Girard (Ann. Chim. anal. 1901, 15, 13).

General properties of the meta-dihydric phenols.—The tendency for the phenols to react in the keto (hydroaromatic) form increases with the entrance of hydroxyl groups in the meta-position. This tendency is therefore exhibited to a greater extent by resorcinol than by phenol



Phenol- form.

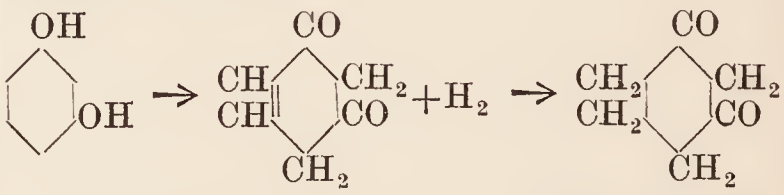


Keto- form.

and is shown to a much greater degree by phloroglucin (*q.v.*).

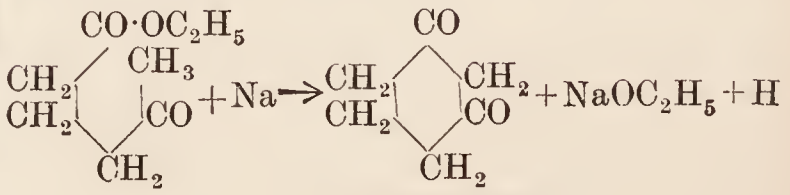
Although the keto- form of resorcinol is not sufficiently stable to cause this substance to react with the usual ketonic reagents (hydroxylamine, &c.), yet there is no doubt that the formation of C-alkyl derivatives by the action of alkyl iodides on the sodium salt of resorcinol (*cf.* Herzig and Zeisel, Monatsh. 1889, 12, 191, 368; Ciamician and Silber, Gazz. chim. ital. 1893, 22, 2, 56) is due to the phenol reacting in its keto- form.

It has, moreover, been found by Merling (Annalen, 1893, 278, 20) that, unlike phenol, resorcinol is readily reduced by sodium amalgam to dihydroresorcin



(Dihydroresorcin.)

a typical alicyclic diketone which has been prepared by Vorländer (Ber. 1897, 28, 2348; Annalen, 1897, 294, 269) by the action of sodium on ethyl-γ-acetobutyrate



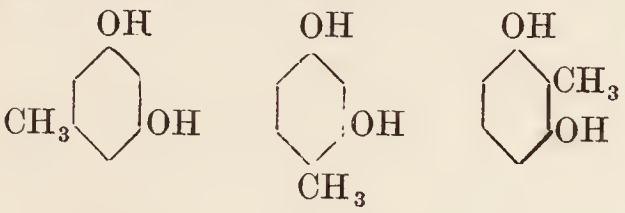
Dihydroresorcin.)

The meta-dihydric phenols also react with aqueous alkaline bicarbonates yielding the salts of hydroxy acids thus—

$$C_6H_4(OH)_2+KHCO_3 \rightarrow C_6H_3(OH)_2\cdot COOK+H_2O$$

(*v.* Kostanecki, Ber. 1885, 18, 3202).

Homologues of resorcinol.—There are three possible dihydroxytoluenes which can be formed by the entrance of a methyl group into the nucleus of resorcinol, namely—



Orcinol (3 : 5-dihydroxy-1-methylbenzene) was discovered by Robiquet in 1829, and is found in many lichens (*Rocella tinctoria, Lecanora*, &c.). It is formed by the elimination of carbon dioxide from orsellinic acid, *e.g.* upon fusing extract of aloes with potash—

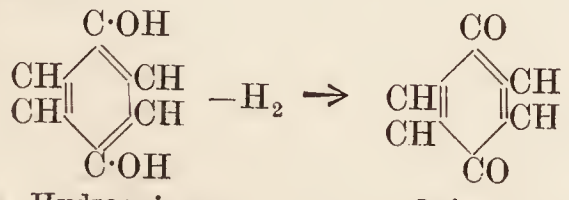
$$C_6H_2(CH_3)(OH)_2COOH \rightarrow C_6H_3(CH_3)(OH)_2+CO_2$$

(Orcinol)

and can also be prepared synthetically from toluene (Ber. 1882, 15, 2992). It is also formed by the action of sodium on ethyl acetonedicarboxylate (*ibid.* 1886, 19, 1446).

Orcinol crystallises from water in prisms containing water of crystallisation which begin to melt at about 56° in their hydrated state; when anhydrous it melts at 107°–108° and boils at 287°–290°. It gives a violet-black coloration with ferric chloride, but does not yield a phthalein when fused with phthalic anhydride. Its alkaline solution, when warmed with chloroform, gives a bright-red liquid which shows a strong yellowish-green fluorescence on dilution (homofluorescein reaction). *Cresorcinol* (2 : 4-dihydroxy-1-methylbenzene, formula II.) melts at 103°–104° and boils at 267°–270°; 2 : 6-*dihydroxy*-1-*methylbenzene*, formula III., melts at 116°–121° and boils at 264°. Both the above compounds give the fluorescein reaction. p-*Xylorcinol* (β-orcinol, 3 : 5-dihydroxy-1 : 4-dimethylbenzene) is formed by the decomposition of barbatic acid, and also by boiling methylenediresorcinol with zinc-dust and aqueous sodium hydroxide (Luther, Arch. Pharm. 1906, 244, 561). It has been prepared synthetically from *p*-xylene (Ber. 1886, 19, 2318; 1916, 49, 621); it melts at 163° and boils at 277°–280°.

Hydroquinone $C_6H_4(OH)_2$ (Quinol, 1 : 4-dihydroxybenzene). The para-dihydroxy derivatives of benzene possess the property of readily losing two atoms of hydrogen in the presence of oxidising agents and passing into quinones (*q.v.*)—



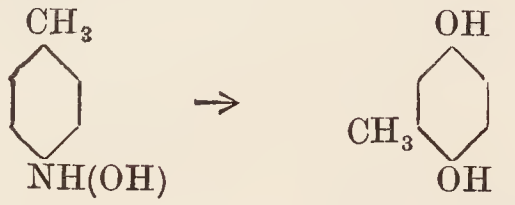
They are therefore named hydroquinones. Hydroquinone was first prepared by Caventou and Pelletier from quinic acid on dry distillation, and was further investigated by Wöhler (Annalen, 1844, 51, 145). It occurs naturally in the sugar-bush (*Protea mellifera*), a shrub of common occurrence in South Africa (Hesse, *ibid.* 1896, 290, 317), and in the buds of the pear tree (*Pyrus communis*). It can be obtained synthetically by a number of processes, of which the following are the more important. From phenol by oxidation with alkaline potassium persulphate (D. R. P. 81068, 1895; Chem. Fabrik. vorm. E. Schering) or with hydrogen peroxide (Henderson and Boyd, Chem. Soc. Trans. 1910, 97, 1666); by fusing *p*-iodophenol with potash (Körner, Zeitsch. Chem. 1866, 662, 731) or by heating *p*-chlorophenol with alkalis in the presence of copper under pressure to a high temperature (D. R. P. 269544); and from *p*-diazophenol sulphate when boiled with 10–15 p.c. sulphuric acid (Weselsky and Schuler, Ber. 1876, 9, 1159). It is also formed when the glucoside arbutin is hydrolysed by boiling dilute sulphuric acid (Kawalier, Annalen, 1852, 84, 358; Strecker, *ibid.* 1858, 107, 228) and is produced by the electrolytic oxidation of benzene in alcohol-sulphuric acid solution (Gattermann and Friedrichs, Ber. 1894, 27, 1942). It has been prepared from ethyl succinate through ethyl succinosuccinate (Hermann, Annalen, 211, 336).

The *preparation* of hydroquinone is best effected by the oxidation of aniline in the following way. A concentrated aqueous solution of sodium dichromate is gradually added to a well-cooled (5°–10°) solution of 1 part of aniline in 8 parts of sulphuric acid and 25 parts of water. The mixture at first becomes green, and towards the end of the operation, deep blue-black; a further addition of the dichromate solution brings about the solution of the greater part of the precipitate, and a brown turbid liquid is obtained containing quinone and quinhydrone in suspension. The quinone and quinhydrone are then reduced to hydroquinone by passing sulphur dioxide through the liquid until it smells of sulphurous acid, the suspended matter is filtered off, and the hydroquinone extracted from the filtrate by means of ether, which is subsequently distilled off. The yield of crude hydroquinone under these conditions amounts to as much as 85 p.c. In order to purify the product it is dissolved in the smallest possible amount of water, the solution boiled with animal charcoal and a little sulphurous acid, filtered and allowed to crystallise.

Hydroquinone is dimorphous. It crystallises from water in colourless hexagonal prisms which, on heating, sublime in monoclinic scales. It melts at 170·3° and boils at 285° (730 mm.); 100 parts of a solution of hydroquinone saturated at 15° contain 5·85 parts of the phenol and it is readily soluble in alcohol, ether, and in hot water. Ferric chloride converts it into quinone and quinhydrone, and an aqueous solution gives no precipitate with lead acetate. Its alkaline solution becomes brown on exposure to the air. It reduces Fehling's solution in the cold and ammoniacal silver nitrate solution on warming, owing to the formation of quinone, and this oxidation to quinone is effected by nitric acid, chlorine or other oxidising agents and also by laccase. When its vapour is passed through a tube heated to redness, it is transformed into quinone and free hydrogen (Hesse, Annalen, 1860, 114, 297). When heated with phthalic

anhydride and sulphuric acid it yields quinizarin, and when heated with phthalic anhydride and zinc chloride it is converted into the colourless hydroquinonephthalein (Grimm, Ber. 1873, 6, 506).

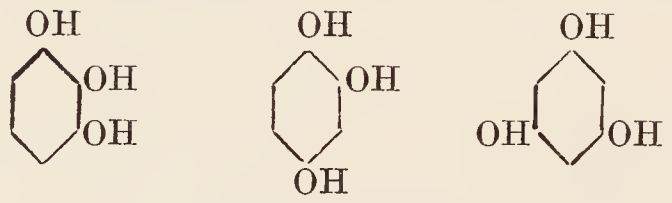
Homologues of hydroquinone are usually named after the parent hydrocarbon. *Toluhydroquinone* $C_6H_3(CH_3)(OH)_2$ (2 : 5-dihydroxy-1-methylbenzene) is of interest because it is formed by the action of hot dilute sulphuric acid on *p*-tolylhydroxylamine (Bamberger, Ber. 1895, 28, 246)—



(Toluhydroquinone.)

It melts at 126°–126·5°. Of the *xylohydroquinones*, the *ortho*-compound melts at 221°, the *meta*-compound at 149°, and the *para*-derivative at 217°.

The trihydric phenols. The three theoretically possible trihydroxy derivatives of benzene are known ; they are



(Pyrogallol.) (Hydroxyquinol.) (Phloroglucinol.)

Pyrogallol $C_6H_3(OH)_3$ (pyrogallic acid, 1 : 2 : 3-trihydroxybenzene) was first prepared by Scheele in 1786 by the dry distillation of gallic acid—

$$C_6H_2(OH)_3COOH \rightarrow C_6H_3(OH)_3+CO_2$$
(Gallic acid.)

and it is by this process that it is prepared commercially at the present day. It is also formed from α- or β-parachlorophenolsulphonic acid by fusion with potash (Petersen and Baehr-Predari, Annalen, 1871, 157, 136). The *preparation* of pyrogallol is usually carried out as follows. Gallic acid is heated with 2–3 times its weight of water in a bronze digester at 200°–210° for about half an hour, the escape of carbon dioxide evolved during the operation being provided for. The resulting almost colourless solution of pyrogallol is then boiled with animal charcoal, filtered, the filtrate rapidly evaporated, and the pyrogallol, which crystallises out, distilled under a pressure of 20–30 mm. The yield is practically theoretical.

In order to obtain the phenol cheaply for photographic purposes, T. E. Thorpe (Chem. News, 43, 109) recommends that 10 grms. of gallic acid and 30 grms. of glycerol be heated at 190°–200° as long as carbon dioxide is evolved. A theoretical yield is obtained and the mass dissolved in a litre of water, gives a solution suitable for photographic work. For the preparation of pyrogallol from 2 : 6-dihalogen-1-phenol-4-sulphonic acids, *cf.* D. R. P. 207374, 1907.

Pyrogallol forms white lustrous needles or thin plates, melts at 132° and boils with partial decomposition at 210°. It is soluble in 2·25 parts of water at 13°, has a bitter taste and is poisonous. It is readily soluble in ether and in alcohol and its alkaline aqueous solution absorbs oxygen from the air, becoming deep-brown in colour. It is upon this property that the employment of an alkaline solution of pyrogallol in gas analysis depends. The absorption of oxygen involves the decomposition of the phenol into carbon dioxide, acetic acid, carbon monoxide and products of high molecular weight (*see* Nierenstein, Chem. Soc. Trans. 1915, 107, 1217) ; allowance must be made for the production of the small quantity of carbon monoxide formed in this manner (see below). Gold, silver, and mercury salts are rapidly reduced by pyrogallol ; a solution of a ferrous salt, free from any trace of ferric salt, produces a white turbidity when added to a solution of pyrogallol, but if any ferric salt be present, a blue coloration is at once formed, which rapidly changes to a brown-red, owing to the oxidation of the pyrogallol by the ferric salt to a product giving a blue colour with ferrous salts (Jacquemin, Compt. rend. 1873, 77, 593). Ferric salts in excess and other oxidising agents, such as potassium permanganate and chromic acid, oxidise pyrogallol to purpurogallin (Wichelhaus, Ber. 1872, 5, 848), a red compound which yields naphthalene on distillation with zinc-dust. When heated with phthalic anhydride, pyrogallol is converted into gallein (*q.v.*) ; it is usual to employ gallic acid in the preparation of this substance since at the high temperature of the reaction it is converted into pyrogallol. Anthragallol is formed when this condensation is effected in the presence of a condensing agent such as excess of strong sulphuric acid (Seuberlich, Ber. 1877, 10, 42).

The employment of pyrogallol in gas analysis.—It has been found that 1 grm. of pyrogallol, dissolved in aqueous potash, is capable of absorbing 189·8 c.c. of oxygen (Liebig, Annalen, 77, 107). Oxygen is most rapidly absorbed by a solution of either 0·25 grm. of pyrogallol in 10 c.c. of aqueous potash of sp.gr. 1·050 (Weyl and Zeitler, Annalen, 1880, 205, 255), or by the same amount of the phenol in 10 c.c. of aqueous caustic soda of sp.gr. 1·030 (Weyl and Goth, Ber. 1881, 14, 2659 ; *see also* Anderson, J. Ind. Eng. Chem. 1915, 7, 587 ; 1916, 8, 131, 133, 999 ; Shipley, J. Amer. Chem. Soc. 1916, 38, 1687). The amount of carbon monoxide evolved is greater with pure oxygen than with a mixture of oxygen and nitrogen, being about 3·5 p.c. with pure oxygen, and 2·5 p.c. with air, of the quantity of oxygen absorbed (Calvert, Cloez and Bousingault, Compt. rend. 57, 873 ; Annalen, 1864, 130, 248).

The ethers of pyrogallol.—The dimethyl ether (pyrogallol dimethyl ether)

$$C_6H_3(OH)(OCH_3)_2, (OCH_3 : OH : OCH_3 = 1 : 2 : 3)$$

occurs in beechwood tar creosote, and can be isolated by treating the fraction boiling at 250°–270° with benzoyl chloride, and subsequently decomposing the crystalline benzoyl derivative (m.p. 118°) with alkali (Hofmann, Ber. 1875, 8, 66 ; 1878, 11, 329 ; 1879, 12, 1371). It has also been prepared by Graebe and Hess (Annalen, 1905, 340, 232) by heating syringic acid at 240°–270°. Methyl trimethylgallate $C_6H_2(O{\cdot}CH_3)_2{\cdot}CO_2{\cdot}CH_3$ also yields this ether when heated under pressure with hydroxides of the alkalis or alkaline earths and water

(D. R. P. 162658). It forms white prisms, melts at 54·8° and boils at 262·7°. When oxidised with nitric acid, ferric chloride, chlorine, sodium nitrite in acid solution, or preferably chromic acid in acetic acid solution, it yields cedriret.

The isomeric dimethyl ether

$$(OH : OCH_3 : OCH_3 = 1 : 2 : 3)$$

has been prepared by heating 2-hydroxy-3 : 4-dimethoxybenzoic acid at 200° (Herzig and Pollak, Ber. 1903, 36, 660). It boils at 232°-234° or 122°–123°/17 mm.

Hydroxyquinol $C_6H_3(OH)_3$ (1 : 3 : trihydroxybenzene) is obtained together with diquinol and δ-hexahydroxydiphenyl, by very rapidly heating hydroquinone with 8–10 times its weight of caustic soda until the evolution of hydrogen has almost ceased (Barth and Schreder, Monatsh. 1883, 4, 176; Herzig and Zeisel, *ibid.* 1888, 9, 149). It crystallises from ether in microscopic scales, melts at 140·5° and distils with partial decomposition into quinol. Its aqueous solution becomes rapidly coloured on exposure to the air, and when treated with a drop or two of aqueous ferric chloride gives a transient bluish-green coloration, which, on the addition of a very small quantity of aqueous sodium carbonate, becomes dark-blue and on the addition of a further amount, wine-red. For an account of the derivatives of hydroxyquinol, compare Bargellini and his collaborators (Gazz. chim. ital. 1910, 40, ii. 342; 1911, 41, ii. 612; 1912, 42, ii. 351; Atti R. Accad. Lincei, 1911, [v.] 20, i. 22; ii. 18, 118, 183) and Ghosh and Watson (Proc. Chem. Soc. 1913, 29, 9). The *trimethyl derivative* 1 : 2 : 4-trimethoxybenzene, boils at 247° and is prepared by the action of dimethyl-sulphate on hydroxyquinol triacetate (Kulka, Chem. Zeit. 1903, 27, 407; Schüler, Arch. Pharm. 1907, 245, 262; Bargellini and Martegiani, Atti R. Accad. Lincei, 1911, [v.] 20, ii. 18). It has been used by Reigrodski and Tambor (Ber. 1910, 43, 1964) for the synthesis of 2 : 3-dioxyflavone.

Phloroglucinol $C_6H_3(OH)_3$ (1 : 3 : 5-trihydroxybenzene) is obtained by fusing with potash certain glucosides, as for example phloretin, whence its name (Hlasiwetz, Annalen, 1855, 96, 120), quercitrin obtained from species of *Quercus* (Hlasiwetz, *ibid.* 1859, 112, 98), maclurin, which, in an impure form, is obtained from fustic (Hlasiwetz and Pfaundler, *ibid.* 1863, 127, 357,) catechin, kino (Hlasiwetz, *ibid.* 134, 118), dragon's blood (Hlasiwetz and Barth, *ibid.* 1865, 134, 283), gamboge (Hlasiwetz and Barth, *ibid.* 1866, 138, 69), and scoparin, a yellow dye obtained from *Spartium scoparum* (Hlasiwetz, *ibid.* 1866, 138, 190). It is also obtained by fusing benzene trisulphonic acid, phenol (Barth and Schreder, Ber. 1879, 12, 422), resorcinol (Barth and Schreder, *ibid.* 1879, 12, 503), or orcinol (Barth and Schreder, Monatsh. 1882, 3, 649) with an excess of caustic soda. It has been prepared synthetically from ethyl malonate by Baeyer (Ber. 1885, 18, 3458; compare also Moore, Chem. Soc. Trans. 1904, 85, 165), and from ethyl acetonedicarboxylate by Jerdan (Chem. Soc. Trans., 1897, 71, 1106). Malonyl chloride and acetone in presence of calcium carbonate yield phloroglucinol and diacetoacetylchloride (Komninos, Bull. Soc. chim. 1918, [iv.] 20, 449).

Preparation.—It may be prepared by fusing resorcinol for about 25 minutes with 6 parts of caustic soda at a gradually increasing temperature until the vigorous evolution of gas, which soon sets in, almost ceases and the mass becomes a bright chocolate colour. The mass is then dissolved in water and the solution acidified with dilute hydrochloric acid, filtered, and extracted with ether; the ether being subsequently distilled off, and the phloroglucinol, which separates as a magma, recrystallised after purification with animal charcoal (Barth and Schreder, *l.c.*).

The product usually contains some resorcinol, which can be removed by heating at 100° and moistening with water from time to time until all the resorcinol has been sublimed (Tiemann and Will, Ber. 1881, 14, 954).

Another method of preparation, in which no diresorcin is formed, consists in converting picric acid into picryl chloride, which is then reduced by tin and hydrochloric acid. The triaminobenzene is not isolated, but the solution of the tin chloride double salt is hydrolysed by boiling with hydrochloric acid (Flesh, Monatsh. 1897, 18, 755).

Phloroglucinol can be completely freed from resorcinol and diresorcin by boiling with a concentrated aqueous solution of potassium bicarbonate. Under these circumstances, the potassium salt of phloroglucinolcarboxylic acid is formed which crystallises in needles, is sparingly soluble in a solution of potassium carbonate and alcohol, and when added to dilute hydrochloric acid gives the free acid which can be extracted with ether. The crystalline acid obtained by evaporating the ether solution eliminates carbon dioxide when boiled with water, pure phloroglucinol remaining in the solution (Will and Albrecht, Ber. 1884, 17, 2103; Will, *ibid.* 1885, 18, 1323; Skraup, Monatsh. 1889, 10, 721; compare also Fraps, Amer. Chem. J. 1900, 24, 270).

According to Brunner (Annalen, 1907, 351, 313), potassium phloroglucinolcarboxylate is formed at the ordinary temperature when a stream of carbon dioxide is passed through a mixture of the phenol and potassium carbonate in glycerol.

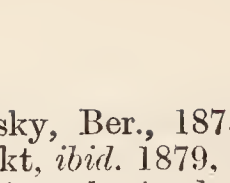
Phloroglucinol crystallises from water in colourless tables containing $2H_2O$, and from ether in large rhombic plates. These lose their water of crystallisation at 100°, forming the anhydrous compound which melts at 217°–219° when rapidly heated, but at 200°–209° when slowly heated (Baeyer, Ber. 1886, 19, 2186). It sublimes without decomposition, has a sweet taste, reduces Fehling's solution, is readily soluble in water, alcohol, and in ether, and, according to Tiemann and Will (*l.c.*), is more readily extracted from a neutral than from an acid solution. It is a dibasic acid (Thiele and Roemer, Zeitsch. physikal. Chem. 1908, 63, 711) and its alkaline solution absorbs oxygen from the air, but less readily than pyrogallol (Weyl and Goth, Ber. 1881, 14, 2673). Its aqueous (concentrated) solution gives a blue-violet colour with ferric chloride.

When potassium nitrate is added to a very dilute solution of phloroglucinol and aniline nitrate, a cinnabar-red precipitate of benzeneazophloroglucinol is formed after a short time

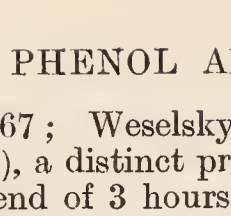
(Weselsky, Ber., 1875, 8, 967; Weselsky and Benedikt, *ibid.* 1879, 12, 226), a distinct precipitate being obtained at the end of 3 hours with only 0·0005 grm. of the substance. A similar reaction is, however, produced by maclurin, decoction of fustic, catechin, and extract of hops (Weselsky, *ibid.* 1876, 9, 217).

Phloroglucinol in the presence of hydrochloric acid gives a red-violet colour with woody substances; thus a solution containing 0·01 p.c. of phloroglucinol colours pine-shavings, moistened with hydrochloric acid, a distinct red, and a solution containing no more than 0·001 p.c. will give this reaction if the shavings are allowed to remain in the solution for 24 hours (Wiesner, Dingl. poly. J. 1878, 227, 397; Kielmeyer, *ibid.* 584; Wagner, *ibid.* 1878, 228, 173). Nierenstein (Collegium, 1906, 14) states that this reaction is also given by resorcinol and pyrogallol. Phloroglucinol solution (1-30000) gives a definite colour with woodpulp paper (Cross, Bevan and Briggs, Ber. 1907, 40, 3119). Unlike pyrogallol, phloroglucinol is not poisonous.

The desmotropism of phloroglucinol.—It has been already stated that the increase in the number of hydroxyl groups in the meta-positions in the benzene nucleus increases the tendency for the compound to react in its desmotropic forms. It is therefore to be expected that in phloroglucinol this tendency would be at its maximum. The experimental facts which show that this phenol reacts in the two desmotropic forms


(Phenol form.)

and


(Keto- form.)

may be summarised as follows:—

The *phenol form* leads to the formation of a tricarbanilido-derivative

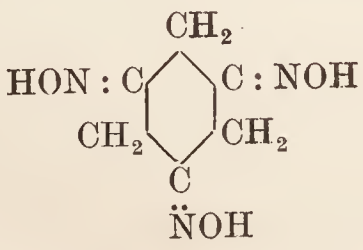
$$C_6H_3(O\cdot CO\cdot NHC_6H_5)_3$$

when phloroglucinol is treated with phenyl*iso*-cyanate (Goldschmidt and Meissler, Ber. 1890, 23, 269; Dieckmann, Hoppe and Stein, Ber. 1904, 37, 4627) and causes the phenol to yield well-defined O-alkyl derivatives of the type

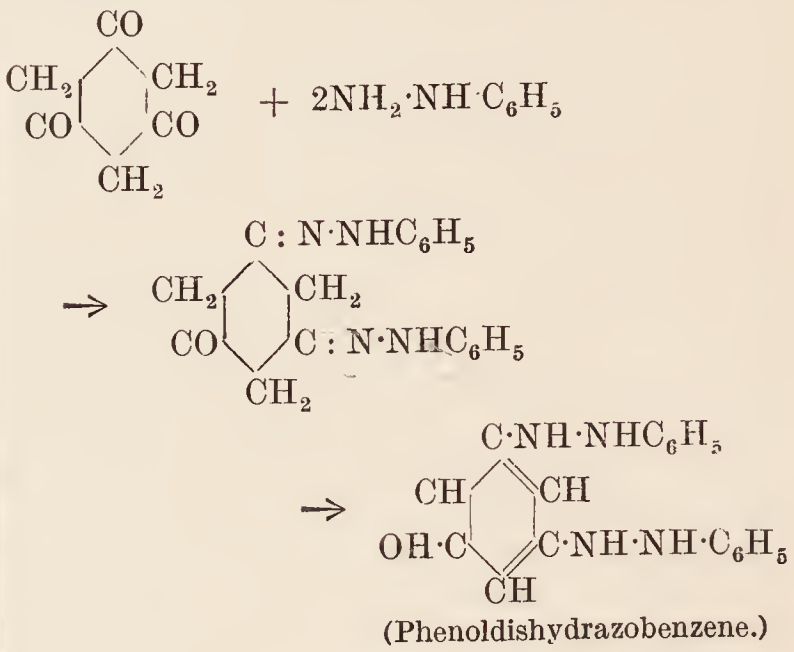
$$C_6H_3(OR)_3$$

when it is alkylated under suitable conditions (Benedikt, Annalen, 1875, 178, 97; Will and Albrecht, Ber. 1884, 17, 2107; Herzig and Zeisel, Monatsh. 1888, 9, 218; Hesse, Annalen, 1893, 276, 328; Herzig and Wenzel, Monatsh. 1906, 27, 781; Nierenstein, Collegium, 1906, 14).

The *keto-form* leads to the production of a *trioxime*

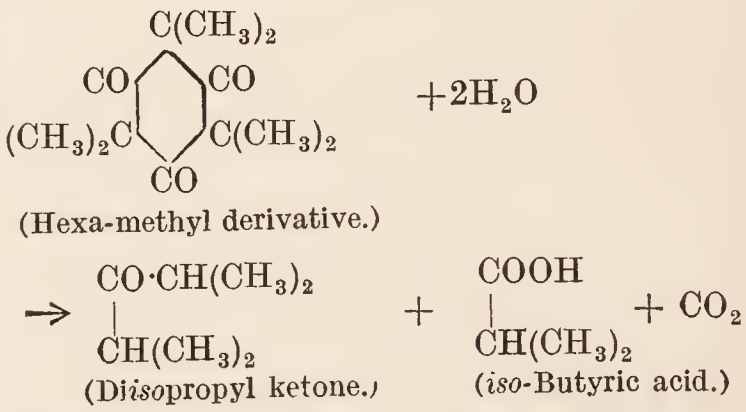


when phloroglucinol is treated with hydroxylamine (Baeyer, Ber. 1886, 19, 159). It is a sandy, crystalline powder which decomposes with explosive violence at 155°. The action of phenylhydrazine leads, in the first instance, to the formation of a salt which on long standing in alcohol passes into phenoldishydrazobenzene

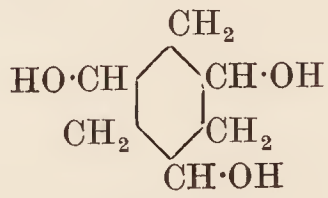

(Phenoldishydrazobenzene.)

(Baeyer and Kochendoerfer, Ber. 1889, 2189). The keto- form is also shown by the readiness with which phloroglucinol reacts with concentrated aqueous ammonia in the cold, yielding, firstly, amino-resorcinol (phloramine, 3 : 5-dihydroxy-1-aminobenzene), and by further action, diaminophenol(5-hydroxy-1 : 3-diaminobenzene), Pollak (Monatsh. 1893, 14, 401).

Tetra-, penta-, and hexa- alkylated products are formed from phloroglucinol when it is alkylated by alkyl iodides in the presence of alcoholic potash. The alkyl groups in these compounds are not removed by hydriodic acid and are therefore attached to carbon. Their constitution may be illustrated by the hexa-methyl derivative which, on heating with concentrated hydrochloric acid at 190°, is transformed into carbon dioxide, di*iso*propyl ketone, and *iso*butyric acid


(Hexa-methyl derivative.)

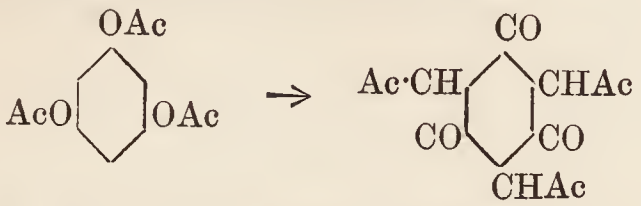
(Herzig and Zeisel, Monatsh. 1888, 9, 217, 882; 1889, 10, 735; 1893, 14, 376). Phloroglucinol is reduced by sodium amalgam in the cold, yielding phloroglucite (*cyclo*-hexanetriol)


(Phloroglucite.)

(W. Wislicenus, Ber. 1894, 27, 357).

The tendency for derivatives of the phenol form to pass into derivatives of the keto- form is illustrated by the behaviour of phloroglucinol-triacetate which, on heating with an equal part

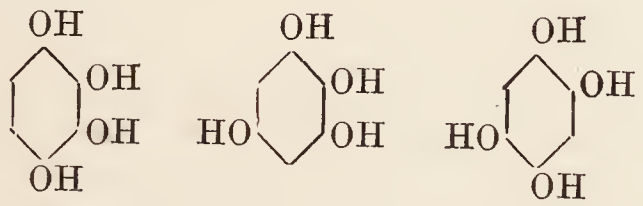
of zinc chloride for 3 hours at 130°, passes into triacetotriketohexamethylene, thus—



(Heller, Ber. 1909, 42, 2736; 1912, 45, 418).

The dynamic isomerism of phloroglucinol is described by Hedley (Chem. Soc. Trans. 1906, 89, 730).

The tetrahydric phenols. There are three theoretically possible tetrahydroxy derivatives of benzene

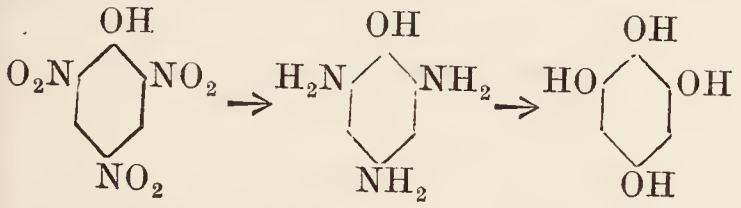


(1 : 2 : 3 : 4) (1 : 2 : 3 : 5) (1 : 2 : 4 : 5)

all of which have been prepared; two of them occur naturally in the form of their ethers.

1 : 2 : 3 : 4-*Tetrahydroxybenzene* (Apionol) is the parent substance of the *apiols* (*v.* Oils, Essential). It has been prepared synthetically by Einhorn, Cobliner and Pfeiffer (Ber. 1904, 37, 119) by the action of water on the hydrochloride of aminopyrogallol. It forms colourless needles from benzene which melt at 161°. The *tetra-acetyl-derivative* forms needles melting at 136°. The phenol is readily soluble in water, alcohol or ether, and dissolves in alkali forming a pale yellow solution which does not absorb oxygen from the air. The aqueous solution gives an intense blue colour with ferric chloride. A *dimethylmethylene* ether $C_6H_3(OCH_3)_2<^{O}_{O}>CH_2$ (apione), melting at 79°, is formed by the oxidation of Petersilien apiol. *Tetramethyl-apionol* $C_6H_2(OCH_3)_4$, melting at 89°, has been prepared by Ciamician and Silber (Ber. 1896, 29, 1808); it is probably identical with the ether prepared from the free phenol and dimethyl sulphate, which melts at 83° (*cf.* Einhorn, Cobliner and Pfeiffer, *l.c.* 105).

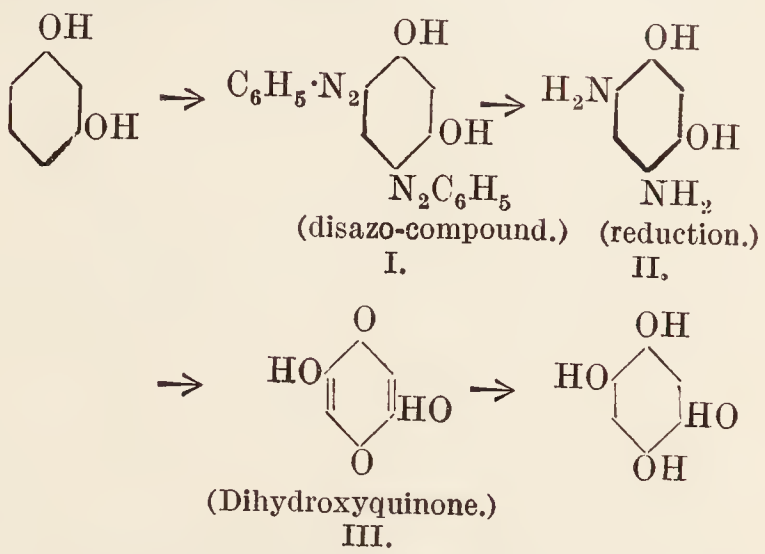
1 : 2 : 3 : 5-*Tetrahydroxybenzene* (oxyphloro-glucinol) is formed from picric acid by reduction and elimination of the amino-groups by boiling the hydrochloride of the amino-compound with water



In the first instance, the trihydroxyamino-benzene $NH_2{\cdot}C_6H_2(OH)_3$ is formed, but on heating with water at 150° the remaining amino-group is eliminated (Will, Ber. 1888, 21, 609, 2020).

The tetrahydric phenol forms slender needles, melting at 165°, and the aqueous solution gives a deep-red colour with ferric chloride. The *monomethyl ether* (2-methoxy-1 : 3 : 5-trihydroxy-benzene, *iretol*), is formed by the decomposition of the glucoside *iridine* (from violet roots); it forms white needles which melt at 186° and are readily soluble in water. The *trimethyl ether* (1 : 2 : 3-trimethoxy-5-hydroxybenzene) has been prepared by Graebe and Suter (Annalen, 1905, 340, 222). It melts at 146° and is identical with Kiliani's antiarol. For other derivatives of this phenol, *see* Bargellini and Bini (Atti R. Accad. Lincei, 1910, [v.] 19, ii. 595).

1 : 2 : 4 : 5-*Tetrahydroxybenzene* is formed from resorcinol in a manner which is indicated by the following scheme :—

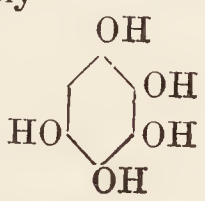


(disazo-compound.) I. (reduction.) II.

(Dihydroxyquinone.) III.

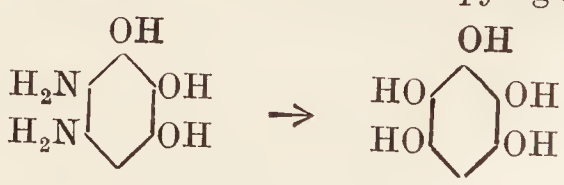
sym-Resorcinoldisazobenzene (I.) is formed by the action of benzene diazonium chloride on resorcinol in the presence of excess of caustic alkali. This is reduced to diaminoresorcinol (II.), which yields diiminoresorcinol on oxidation, a substance which is converted into dihydroxy-quinone (III.) on treatment with caustic alkali; the last-named compound is reduced to the tetrahydric phenol by stannous chloride. The tetrahydroxybenzene forms glistening leaflets which melt between 215° and 220°; the aqueous solution becomes rapidly brown on exposure to the air and is at once oxidised to dihydroxy-quinone by ferric chloride.

Pentahydric phenol. There is only one theoretically possible pentahydroxy derivative of benzene, namely—



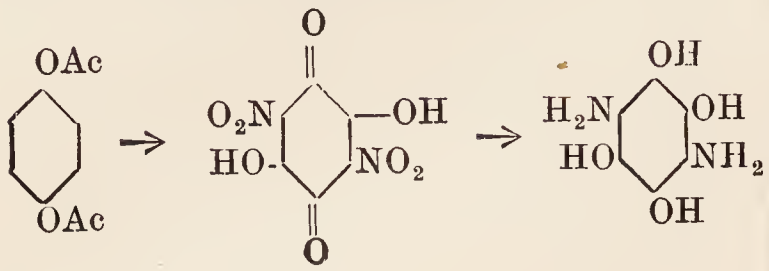
(1 : 2 : 3 : 4 : 5)

1 : 2 : 3 : 4 : 5-*Pentahydroxybenzene.* A substance having this constitution has been described by Wenzel and Weidel (Chem. Zentr. 1903, ii. 829) as forming colourless crystals insoluble in all the usual organic solvents. Different properties are given to this compound by Einhorn, Cobliner and Pfeiffer (Ber. 1904, 37, 122), who prepared it by the action of water on the hydrochloride of 4 : 6-diaminopyrogallol

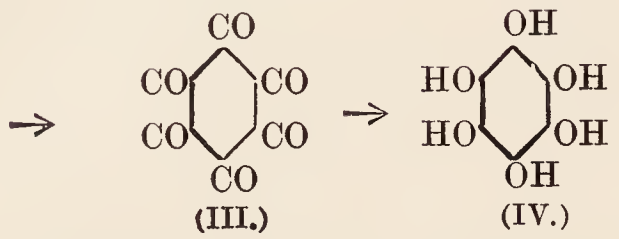


It forms microscopic needles when crystallised from benzene which are readily soluble in ether, alcohol, or ethyl acetate, and which blacken when heated. The aqueous solution gives a dark-red brown colour with ferric chloride. The *penta-acetyl derivative* forms colourless needles which melt with decomposition at 165°.

The only *hexahydric phenol*, hexahydroxybenzene $C_6(OH)_6$, has been prepared by Nietzki and Benckiser (Ber. 1885, 18, 499, 1833) from the diacetyl derivative of hydroquinone in the following way:—



(I.) (II.)



(III.) (IV.)

The diacetyl derivative is converted into the so-called 'nitranilic acid' (I.) by the action of nitric and sulphuric acids; this is then reduced to diaminotetrahydroxybenzene (II.) which is oxidised by means of nitric acid to triquinoyl (III.); the latter is then reduced by stannous chloride to hexahydroxybenzene (IV.). The hexahydric phenol forms long needles which cannot be obtained completely colourless; when heated it becomes dark-grey at about 200° without melting. It is sparingly soluble in cold water, but readily dissolves on warming, and is sparingly soluble in alcohol, ether, or benzene. The aqueous solution becomes quickly red-violet on exposure to the air and at once reduces silver nitrate. It is oxidised by concentrated nitric acid to triquinoyl and when its alkaline solution is treated with air, it is converted into tetrahydroxyquinone. The action of dilute alkali yields potassium croconate, and acetic anhydride produces the *hexa-acetyl* derivative which melts at 203° (Maquenne, Bull. Soc. chim. 1887, [ii.] 48, 64). The potassium salt of hexahydroxybenzene is identical with 'potassium carboxide,' which is prepared by the action of dry carbon monoxide on melted potassium (Gmelin, Pogg. Ann. 1825, 4, 35). J. F. T.

PHENOL COLOURING MATTERS *v.* OXAZINE COLOURING MATTERS.

PHENOL CORALLIN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PHENOLAX. Trade name for phenolphthalein used as a laxative.

PHENOLPHTHALEÏN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PHENOPHENANTHRAZINE *v.* AZINES.

PHENOSAFRANINE *v.* AZINES.

PHENOSTAL. Trade name for diphenyl oxalate $(COOC_6H_5)_2$ used as an antiseptic.

PHENOVAL. Trade name for bromo*iso*valeryl, *v. p*-PHENETIDINE.

PHENYFORM $C_6H_4(OH)(CH_2OH)xCH_2O$ (?). A greyish-white powder used as an antiseptic. *v.* SYNTHETIC DRUGS.

PHENYL. Under this heading will be described the monosubstituted derivatives of benzene, having the general formula C_6H_5R. The radicle C_6H_5 is known as phenyl and is monovalent.

Aminobenzene *v.* ANILINE.

Bromobenzene, *Phenyl bromide* C_6H_5Br. Prepared by the interaction of benzene and bromine in the presence of sunlight (Schramm, Ber. 1885, 18, 606), iodine (Rilliet and Ador, *ibid.* 1875, 8, 1287), aluminium chloride (Leroy, Bull. Soc. chim. 1887, 48, 211; Greene, Compt. rend. 90, 40), or aluminium amalgam (Cohen and Dakin, Chem. Soc. Trans. 1899, 894); by the action of phenylhydrazine on perbromacetone (Levy and Jedlicka, Annalen, 249, 84); by the action of sulphur bromide and nitric acid on benzene (Edinger and Goldberg, Ber. 1900, 33, 2884); by diazotising aniline in the presence of copper, sulphuric acid, and potassium bromide (Sandmeyer, *ibid.* 1884, 17, 2650); for electrolytic method *v.* Votoček and Zenišek (Chem. Zentr. 1899, i. 1146).

For the influence of sulphur and sulphur containing groups on the order of substitution of hydrogen atoms in benzene hydrobromide, *see* Bourgeois and Abraham (Rec. trav. chim. 1911, 30, 407).

Bromobenzene is a colourless liquid, b.p. 156·6° (758·6 mm.) (Feitler, Zeitsch. physikal. Chem. 4, 70); m.p. −30·5° (corr.) (Schneider, *ibid.* 22, 232; *cf.* Haase, Ber. 1893, 26, 1053); sp.gr. 4°/4° 1·5105, 15°/15° 1·4991, 25°/25° 1·4886, 50°/50° 1·4681, 100°/100° 1·4416; magnetic rotation (Perkin, Chem. Soc. Trans. 1896, 1243); vapour pressure (Ramsay and Young, *ibid.* 1885, 646, 655; Young, *ibid.* 1889, 488, 506; Kahlbaum, Zeitsch. physikal. Chem. 26, 584); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911, 811); dielectric constant (Jahn and Möller, Zeitsch. physikal. Chem. 13, 386). Heated with aluminium chloride, bromobenzene yields benzene and isomeric dibromobenzenes (Dumreicher, Ber. 1882, 15, 1867); with sodium methoxide at 200° anisole, phenol, and a small quantity of benzene are formed (Blau, Monatsh. 7, 626). Sodium in ether yields hydrocarbons of high molecular weight and a dark-blue substance (Weiler, Ber. 1896, 29, 115; Mohr, J. pr. Chem. 1909, [ii.] 80, 315); ethyl oxalate and sodium in absolute ether yield benzoic acid and triphenylcarbinol (Frey, Ber. 1895, 28, 2315). Heated with sulphuric acid, bromobenzene yields 1 : 3 : 5-dibromobenzene sulphonic acid and a bromobenzene disulphonic acid (Herzig, Monatsh. 2, 192); nitric acid (sp.gr. 1·5) gives 1 : 2 : 4-bromodinitrobenzene together with *o*- and *p*-bromonitrobenzenes (Bandrowski, Bull. Acad. Sci. Cracow, 1900, 193). Hydriodic acid and phosphorus are without action on bromobenzene at 218° (Klages and Liecke, J. pr. Chem. [ii.] 61, 319).

Chlorobenzene, *Phenyl chloride,* C_6H_5Cl. Prepared by the action of phosphorus pentachloride on phenol (Gerhardt and Laurent, Annalen, 75, 79); by heating benzene with thionyl chloride at 150° (Dubois, Zeitsch. Chem. 1866, 705) or with sulphur chloride at 250° (Schmidt, Ber. 1878, 11, 1173); by heating nitrobenzene with thionyl chloride at 160°–180° (H. Meyer, Monatsh. 1915, 36, 719); by the electrolysis of a strong hydrochloric acid solution of cupric chloride in the presence of benzene diazonium chloride using copper electrodes (Votoček and Zenišek, Chem. Zentr. 1899, i. 1146; *cf.* Walter, J. pr. Chem. 1896, [ii.] 53, 427); by diazotising aniline and heating

the product with cuprous chloride (Sandmeyer, Ber. 1884, 17, 1633); by the action of chlorine on benzene in the presence of aluminium chloride (Mouneyrat and Pouret, Compt. rend. 1898, 127, 1026), ferric chloride (Thomas, *ibid.* 1898, 126, 1212), or a mixture of finely divided iron and ferric chloride (D. R. P. 219242; J. Soc. Chem. Ind. 1910, 619).

On the large scale iron only is used, but many other catalysts have been suggested, *e.g.* the chlorides of molybdenum and vanadium and the aluminium mercury couple, as laboratory processes. For details and figures of chlorination plant, *see* Cain's 'Intermediate Products for Dyes,' p. 6 *et seq.* In the chlorination of benzene in the presence of iron the yield of monochlorobenzene increases with the velocity of chlorination. For a given time and a given concentration the fraction of a molecule of benzene converted into mono-chlorobenzene is 8·5 times greater than the fraction of a molecule of chlorobenzene converted into *p*-dichlorobenzene. The yield of mono-chlorobenzene decreases slightly with rise of temperature (Bourion, Compt. rend. 1920, 170, 1319).

Chlorobenzene is a colourless liquid, b.p. 131·8° (757 mm.) (Perkin, Chem. Soc. Trans. 1896, 387; *cf.* Ramsay and Young, *ibid.* 1885, 642, 654; Fuchs, Zeitsch. angew. Chem. 1898, 869); m.p. −45° (corr.) (Schneider, Zeitsch. physikal. Chem. 19, 155); sp.gr. 4°/4° 1·1230, 15°/15° 1·1125, 25°/25° 1·1042, 50°/50° 1·0868, 100°/100° 1·0623 (Perkin, *l.c.*); critical temperature 359·2° (Young, Zeitsch. physikal. Chem. 11, 590; Schneider, *ibid.* 70, 626); vapour pressure (Young, Chem. Soc. Trans. 1889, 90, *et seq.*); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911, 811); magnetic rotation (Perkin, *l.c.*); dielectric constant (Jahn and Möller, Zeitsch. physikal. Chem. 13, 387). By passing the vapour of chlorobenzene over red-hot iron filings, diphenyl, mono- and di- chlorodiphenyl and diphenylbenzene are formed (Kramers, Annalen, 189, 135). On heating with sodium in carbon tetrachloride, triphenylmethane, hexaphenylbenzene and diphenyl are produced (Schmidlin, Compt. rend. 1903, 137, 59), whilst with aluminium chloride the products are the chlorides of 4 : 4′- and 2 : 4′-dichlorobenzophenones (Norris and Green, Amer. Chem. J. 1901, 26, 492; Norris and Tweig, *ibid.* 1903, 30, 392). Chlorine in the sunlight yields $C_6H_5Cl{\cdot}Cl_4$, $C_6H_4Cl_8$, and other products; in the presence of dilute sodium hydroxide, *α*- and *β*-chlorobenzene hexachlorides are produced (Matthews, Chem. Soc. Trans. 1891, 167; 1892, 103). Bromine in the presence of aluminium chloride yields *p*-chlorobromobenzene and other products (Mouneyrat and Pouret, Compt. rend. 1899, 129, 605); sulphuric acid and iodine yield chlorodiiodobenzene ($Cl : I_2 = 1 : 2 : 4$), chlorotriiodobenzene ($Cl : I_3 = 1 : 2 : 4 : 6$) and other products (Istrati, Chem. Zentr. 1897, i. 1161). Chlorobenzene remains unchanged on heating with hydriodic acid and phosphorus at 302° (Klages and Liecki, J. pr. Chem. [ii.] 61, 319). Nitric acid at 0° gives *o*-, *m*-, and *p*-

chloronitrobenzenes, the yields being 29·8, 0·3 and 69·9 p.c. respectively (Holleman, Proc. K. Akad. Wetensch. Amsterdam, 1904, 7, 266). Holleman gives a table by which the relative proportions of the *o*- and *p*-compounds may be estimated by determining the m.p. *o*-chloronitrobenzene melting at 32·09° and the *p*-isomeride at 82·15°. The separation of the two isomerides may be effected by a combined process of crystallisation and distillation (Chemische Fabrik Griesheim, D. R. P. 97013; Marckwald, D. R. P. 137847). B.p. at 753 mm. ortho −245·5°, para −238·5°. Oxidised by sulphuric acid and manganese dioxide to formic and *p*-chlorobenzoic acids. Has been recommended as a solvent for resins (Andès, Chem. Rev. Fett. Harz-Ind. 1906, 13, 32). For stability of halogenated benzenes *v.* Löwenherz (Zeitsch. physikal. Chem. 1899, 29, 401); Vandevelde (Chem. Zentr. 1898, i. 438).

Iodobenzene, *Phenyl iodide* C_6H_5I. Prepared by the action of phosphorus triiodide on phenol (Scrugham, Annalen, 92, 318); by heating a mixture of benzene and iodine with aluminium chloride (Green, Compt. rend. 90, 40), ferric chloride (Meyer, Annalen, 231, 195), or with sulphuric acid (Neumann, *ibid.* 241, 84; Istrati and Georgescu, Chem. Zentr. 1892, i. 625), in the last method higher halogenated compounds also being formed; by the interaction of benzene and sulphur iodide in the presence of nitric acid (Edinger and Goldberg, Ber. 1900, 33, 2876); by heating phenyl hydrazine with excess of iodine in potassium iodide solution (Meyer, J. pr. Chem. [ii.] 36, 115); by heating benzene with potassium iodate and dilute sulphuric acid (Peltzer, Annalen, 136, 197); by heating sodium benzoate with iodine monochloride (Schützenberger, J. 1861, 349; 1862, 251).

Iodobenzene is a colourless liquid, b.p. 188·36° (755·75 mm.) (Feitler, Zeitsch. physikal. Chem. 4, 71); m.p. −28·5° (corr.) (Schneider, *ibid.* 19, 157; *cf.* Haase, Ber. 1893, 26, 1053); sp.gr. 4°/4° 1·8551, 15°/15° 1·8401, 25°/25° 1·8283, 50°/50° 1·8067, 100°/100° 1·7832 (Perkin, Chem. Soc. Trans. 1896, 1243); vapour pressure (Young, *ibid.* 1889, 490, 510); heat of combustion 770·0 Cal. (Berthelot, Compt. rend. 130, 1098); magnetic rotation (Perkin, *l.c.*); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911, 2318). Iodobenzene is reduced to benzene by sodium amalgam in alcohol; with aluminium chloride it yields benzene, isomeric diiodobenzenes, hydrochloric acid and iodine (Dumreicher, Ber. 1882, 15, 1868); with silver nitrate at 145° picric acid is formed (Geuther, Annalen, 245, 100); oxidised by Caro's acid to iodoxybenzene (Bamberger and Will, Ber. 1900, 33, 534). Nitric acid (sp.gr. 1·5) yields *o*- and *p*-nitroiodobenzenes (Korner, Gazz. chim. ital. 4, 305); chlorine in chloroform solution gives a dichloride (Willgerot, J. pr. Chem. [ii.] 33, 155). Iodobenzene is unchanged by heating with hydriodic acid and phosphorus at 182° (Klages and Liecke, *ibid.* 61, 319); action of ferric chloride and ferric bromide *v.* Thomas (Compt. rend. 128, 1577).

Nitrobenzene *v.* BENZENE.

Phenyl azoimide, Triazobenzene, Diazobenzeneimide $C_6H_5N_3$. Prepared by the action of ammonia (Greiss, Annalen, 137, 68) or of phenylhydrazine (Oddo, Gazz. chim. ital. 20, 798) on diazobenzene perbromide; by the action of nitrous acid on phenylhydrazine at 0° (Dimroth,

Ber. 1902, 35, 1032); by passing nitrosyl chloride into a solution of phenylhydrazine in glacial acetic acid (Tilden and Millar, Chem. Soc. Trans. 1893, 257); by heating nitrosophenylhydrazine with dilute potassium hydroxide (E. Fischer, Annalen, 190, 92) or with alcoholic hydrochloric acid (O. Fischer, Ber. 1886, 19, 2995); by the interaction of stannous chloride and diazobenzene chloride in hydrochloric acid solution (Culmann and Gasiorowski, J. pr. Chem. [ii.] 40, 99), or of diazobenzene sulphate and sodium azide or hydrazine (Noelting and Michel, Ber. 1893, 26, 86, 89); by the action of sodium hypochlorite on phenylsemicarbazide or on phenylazocarbonamide (Darapsky, *ibid.* 1907, 40, 3033); or together with other products, by the interaction of phenylhydroxylamine and hydroxylamine in the presence of a mineral acid (Bamberger, *ibid.* 1902, 35, 3895).

Phenyl azoimide is a pale yellow oil having an aromatic-ammoniacal smell, b.p. 73·5° at 22–24 mm.; sp.gr. 0°/4° 1·12399 (Oddo), 10°/10° 1·0980, 25°/25° 1·0853 (Perkin, Chem. Soc. Trans. 1896, 1245); insoluble in water, soluble in alcohol or ether. Explodes on distillation at atmospheric pressure. On heating with concentrated hydrochloric acid, it decomposes into nitrogen and *o*- and *p*-chloroanilines (Greiss, Ber. 1886, 19, 313). Strong sulphuric acid causes explosions, but very dilute acid yields *p*-aminophenol. Excess of bromine gives tribromoaniline (Culmann and Gasiorowski, J. pr. Chem. [ii.] 40, 97). Reduction in alcoholic solution with sodium amalgam gives hydrazobenzene (Curtius, *ibid.* [ii.] 52, 210); with zinc and hydrochloric acid ammonia and aniline. Hydrazine hydrate yields benzene, ammonia and nitrogen (Curtius and Dedichen, *ibid.* [ii.] 50, 252). Phenyl azoimide yields triazo compounds by condensation with substances containing a reactive methylene group (Dimroth, Ber. 1902, 35, 4041); it reacts with alkyl magnesium halides forming diazoamino compounds (Dimroth, *ibid.* 1903, 36, 909).

Phenylcarbimide, Phenyl *iso*cyanate, Carbanil $C_6H_5N:C:O$. Prepared by distilling oxanilide (Hofmann, Annalen, 74, 33), diphenylurea (J. 1858, 348) or phenylurethane (Ber. 1870, 3, 655) with phosphorus pentoxide; by distilling oxanilyl chloride (Aschan, *ibid.* 1890, 23, 1825); by heating phenylthiocarbimide with mercuric oxide (Kühn and Liebert, *ibid.* 1536); by decomposing diazobenzene sulphate with potassium cyanate and copper powder (Gattermann, *ibid.* 1225; 1892, 25, 1086); by passing phosgene over fused diphenylurea or better over fused aniline hydrochloride (Hentzchel, *ibid.* 1884, 17, 1284; *cf.* D. R. P. 19919; Frdl. i. 578).

Phenylcarbimide is a colourless liquid, the vapour of which excites tears; b.p. 166° at 769 mm. (Hofmann, Ber. 1885, 18, 764); sp.gr. 1·092 at 15°. With water it yields diphenylurea, with alcohol phenylurethane, and with ammonia monophenylurea. It is much used as a reagent for detecting the presence of hydroxyl and imino groups: condensation with alcohols (*v.* Hofmann, Annalen, 74, 16; Ber. 1871, 4, 249; Tessmer, *ibid.* 1885, 18, 968; 1886, 19, 2606; Snape, Chem. Soc. Trans. 1885, 770; Gumpert, J. pr. Chem. [ii.] 32, 278; Bloch, Bull. Soc. chim. [iii.] 31, 49, 71); with phenol (*v.* Leuckhart and Schmidt, Ber. 1885, 18, 2338). By heating with dilute hydrochloric acid, ammonium chloride, aniline, and carbon dioxide are produced; with acetic acid, diphenylurea, and traces of aniline and acetanilide (Dieckmann and Kammerer, *ibid.* 1907, 40, 373); with acetic anhydride at 170° acetanilide, benzene and carbon dioxide (Gumpert, J. pr. Chem. [ii.] 31, 121); with potassium acetate at 100° triphenyl-*iso*cyanurate (Hofmann, Ber. 1885, 18, 765). It combines with prussic acid in benzene after the addition of a few drops of pyridine to form cyanoformanilide (Dieckmann and Kammerer, *ibid.* 1905, 38, 2977), and with hydrogen chloride to give chloroformanilide (Hentzchel, *ibid.* 1885, 18, 1178). Heated in sealed tubes at 180° it yields carbodiphenylimide (Stollé, *ibid.* 1908, 41, 1125); heated with zinc it gives aniline. It combines with two atoms of chlorine or bromine. With benzene in the presence of aluminium chloride it gives benzanilide (Leuckhart, *ibid.* 1885, 18, 873; J. pr. Chem. [ii.] 41, 301).

Phenyl cyanide, benzonitrile *v.* NITRILES.

Phenyl *iso*cyanide, Phenylcarbylamine *v.* NITRILES.

Phenylhydroxylamine *v.* HYDROXYLAMINE.

Phenylthiocarbimide, Phenyl *iso*thiocyanate, Phenyl mustard oil $C_6H_5N:C:S$. Prepared by heating diphenylthiourea with phosphorus pentoxide (Hofmann, J. 1858, 349), concentrated hydrochloric acid (Weith and Merz, Zeitsch. Chem. 1869, 589), phosphoric acid (Hofmann, Ber. 1882, 15, 986), acetic anhydride (Werner, Chem. Soc. Trans. 1893, 400), or with phthalic anhydride (Dunlap, Amer. Chem. J. 1896, 18, 332), in the last method phthalanilic acid also being formed. By heating phenyl *iso*cyanide with sulphur (Weith, Ber. 1873, 6, 211), phenyl thiohydantoin with carbon disulphide (Dixon, Chem. Soc. Trans. 1897, 628) or phenyl carbimide or phenylurethane with phosphorus pentasulphide at 160° (Michael and Palmer, Amer. Chem. J. 6, 258); by the interaction of thiophosgene and aniline (Rathke, Ber. 1870, 3, 861); together with the hydriodide of triphenylguanidine and aniline by heating an alcoholic solution of diphenylthiourea with iodine (Hofmann, *ibid.* 1869, 2, 453; Rudnew, J. Russ Phys. Chem. Soc. 10, 184).

Phenylthiocarbimide is an unpleasant smelling liquid, b.p. 221° (corr.); sp.gr. 4°/4° 1·1477, 15°/15° 1·1382, 25°/25° 1·1314 (Perkin, Chem. Soc. Trans. 1896, 1204). By boiling with water diphenylthiourea, sulphuretted hydrogen and carbon dioxide are produced (Bamberger, Ber. 1881, 14, 2462); glacial acetic acid at 130° yields acetanilide, carbon oxysulphide, and diphenylurea (Werner, Chem. Soc. Trans. 1891, 548; Claus and Völtzknow, Ber. 1881, 14, 445; Gumpert, J. pr. Chem. [ii.] 32, 294; Cain and Cohen, Chem. Soc. Trans. 1891, 327); whilst with thioacetic acid it gives acetanilide. It combines with ammonia and substituted amines yielding substituted thioureas. Chlorine forms an addition product; copper powder at 200° yields benzonitrile. Reduction with hydrochloric acid in absolute alcohol gives aniline and thioformaldehyde (Pinner, Ber. 1881, 14, 1083), whilst aluminium amalgam in neutral solution gives diphenylthiourea and methyl mercaptan (Gutbier, *ibid.* 1901, 34, 2033). Sulphuric acid

gives carbon disulphide and diphenylthiourea (Proskauer and Sell, *ibid.* 1876, 9, 1266); malonic acid yields diphenylurea and acetanilide, succinic acid succinanil, and sebacic acid, the dianilide of the acid (Bénech, Compt. rend. 130, 292). By condensing phenylthiocarbimide with aliphatic monohydroxyalcohols, phenylthiourethanes are produced (Hofmann, Ber. 1870, 3, 772; Orndorff and Wheeler, Amer. Chem. J. 1899, 22, 458), with phenol phenyl-ψ-phenylthiocarbamic acid (Dixon, Chem. Soc. Trans. 1890, 268; Snape, *ibid.* 1896, 98) and with aromatic hydrocarbons or phenol ethers substituted thioureas (Gattermann, J. pr. Chem. 1899, [ii.] 59, 572). Bromine and alcohol in ethereal solution give a dibromo additive compound and phenylthiocarbimide oxide (Fromm and Heyden, Ber. 1909, 42, 3800; Freund and Bachrach, Annalen, 285, 184; Hantzsch and Wolverkampf, *ibid.* 331, 265).

Phenylthiocyanate, $C_6H_5S{\cdot}C{:}N$. Prepared by the action of thiocyanic acid (Billeter, Ber. 1874, 7, 1753) or of cuprous thiocyanate (Gattermann and Haussknecht, *ibid.* 1890, 23, 739) on diazobenzene sulphate; by passing cyanogen chloride into an alcoholic solution of the lead salt of thiophenol (Billeter, *l.c.*).

It is a colourless liquid having a leek-like smell, b.p. 231° (corr.); sp.gr. 1·155 at 17·5°. Concentrated hydrochloric acid at 180°–200° yields thiophenol, ammonia, and carbon dioxide; alcoholic potassium hydrosulphide gives thiophenol.

PHENYLACETIC ACID, *α-toluic acid*

$$C_6H_6{\cdot}CH_2{\cdot}CO_2H$$

is prepared by the hydrolysis of benzyl cyanide (Cannizzaro, Annalen, 1855, 96, 247; Mann, Ber. 1881, 14, 1645; Staedel, *ibid.* 1886, 19, 1949). It has been obtained by fusing phenylmalonic acid (Wislicenus, *ibid.* 1894, 27, 1094); by boiling vulpic acid with baryta (Möller and Strecker, Annalen, 1860, 113, 64); by fusing atropic acid with potassium hydroxide (Kraut, *ibid.* 1868, 148, 242); by reducing mandelic acid (Brown, Zeitsch. Chem. 1865, 443); by heating phenylchlorovinyl ethyl ether with alcoholic potassium hydroxide (Nef, Annalen, 1899, 308, 318); and by decomposing by water the product of the action of carbon dioxide on an ethereal solution of magnesium benzyl chloride (Zelinsky, Ber. 1902, 35, 2692). It occurs together with phenylpropionic acid among the putrefactive decomposition products of certain proteins (Salkowski, Ber. 1879, 12, 649; Zeitsch. physiol. Chem. 1888, 2, 420; 1892, 9, 507), and the two are readily separated by the fractional crystallisation of the zinc salts (Salkowski, *ibid.* 1892, 10, 150). According to Engler and Löw (Ber. 1893, 26, 1436) the presence of benzenoid hydrocarbons in mineral oil may not be exclusively due to a pyrogenetic process, but may arise from the phenylacetic acid produced by the decay of proteid matter.

Phenylacetic acid crystallises in thin leaves, m.p. 76·5°, b.p. 265·5° (corr.), 144·2°–144·8°/12 mm. (Anschutz and Berns, Ber. 1887, 20, 1390), sp.gr. 1·0778 at 83°, 1·0334 at 135°/4° (Möller and Strecker, *l.c.*), or 1·228 at 4° (Schröder, Ber. 1879, 12, 1612); the magnetic rotatory power is 12·743 (Perkin, Chem. Soc. Trans. 1896, 1079); and the molecular heat of combustion 933·2 Cal. (Stohmann, Kleber and Langbein, J. pr. Chem. 1889, [ii.] 40, 128). In its physiological action phenylacetic acid differs markedly from phenylpropionic acid which is completely oxidised to benzoic acid when administered as a food to a dog, whilst phenylacetic acid is converted under similar conditions into *phenaceturic acid* $C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, m.p. 143° (E. and H. Salkowski, Ber. 1879, 12, 653). When fed to fowls phenylacetic acid combines with ornithine to produce *phenylaceto-ornithuric acid*

$$C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}NH[CH_2]_2CH(NH{\cdot}CO{\cdot}CH_2{\cdot}C_6H_5)CO_2H$$

(Totani, Zeitsch. physiol. Chem. 1910, 68, 75).

Salts.—Calcium salt $(C_8H_7O_2)_2Ca,3H_2O$ (Kraut, *l.c.*); barium salt $(C_8H_7O_2)_2Ba,3H_2O$ loses $2\frac{1}{2}H_2O$ at 150°; lead salt

$$(C_8H_7O_2)_2Pb,H_2O$$

(Guye, J. 1884, 468); silver salt $C_8H_7O_2Ag$; yttrium salt $(C_8H_7O_2)_3Y,3H_2O$ is insoluble (Pratt and James, J. Amer. Chem. Soc. 1911, 33, 1330); the brucine salt

$$C_{23}H_{26}O_4N_2{\cdot}C_8H_8O_2,1\tfrac{1}{2}H_2O$$

has m.p. 130°–131°, $[\alpha]_D^{20°}$ −30·5° in 5 p.c., and −32·2° in $2\frac{1}{2}$ p.c. chloroform solution (Hilditch, Chem. Soc. Trans. 1908, 1388).

Esters.—Methyl ester, b.p. 220°, sp.gr. 1·044 at 16° (Radzisjewski, Ber. 1869, 2, 208); chloromethyl ester, b.p. 138°–140°/15 mm. (Descudé, Compt. rend. 1902, 134, 716); ethyl ester, b.p. 227·3°, sp.gr. 1·0555 at 4°/4°; 1·0462 at 15°/15°, or 1·039 at 25°/25° (Perkin, Chem. Soc. Trans. 1896, 69, 1238); propyl ester, b.p. 238°, sp.gr. 1·0142 at 18° (Hodgkinson, *ibid.* 1880, 34, 483); *iso*butyl ester, b.p. 247° (Hodgkinson, *l.c.*); active amyl ester, b.p. 265°–266°/722·7 mm., sp.gr. 0·982 at 20°/4°; n_D 1·4872 at 21°; $[\alpha]_D$+3·84° at 22° (Guye and Chavanne, Bull. Soc. chim. 1896, [iii.] 15, 292); cyclo Hexyl ester, b.p. 180·5°, D_4^0 1·0535, n_D^{13} 1·518, *o*-methyl-*cyclo*-hexyl ester, b.p. 186°, D_4^0 1·0374 n_D^{13} 1·512; the *m*-isomeride b.p. 188° D_4^0 1·0323, n_D^{13} 1·510; the *p*-isomeride b.p. 188·5°, D_4^0 1·0316, n_D^{13} 1·509; octanyl ester, b.p. 195°/35, D_4^{14} 0·9503 (Senderens and Aboulenc, Compt. rend. 1912, 155, 1254; 1913, 156, 1620); benzyl ester b.p. 317°–319°, sp.gr. 1·101 (Slawik, Ber. 1874, 7, 1056), b.p. 270°/160 mm., sp.gr. 1·0938 at 170° (Hodgkinson, *l.c.*); menthyl ester, b.p. 192°–197°/10 mm.; sp.gr. 1·002 at 20°/4°; 0·9400 at 100°/4°; $[\alpha]_D$−68·70° at 20° (Tschugaeff, Ber. 1898, 31, 2451; Cohen and Dudley, Chem. Soc. Trans. 1910, 1749); b.p. 205·5°/25 mm. D_4^{17} 0·9887 (Senderens and Aboulenc, *l.c.*); phenyl ester, m.p. 42°, b.p. 158°/17 mm. (Stoermer and Biesenbach, Ber. 1905, 38, 1958); phenylethyl ester, m.p. 28°, b.p. 330° (von Soden and Rojahn, *ibid.* 1900, 33, 1720).

Phenylacetyl chloride $C_6H_5{\cdot}CH_2{\cdot}COCl$ has b.p. 95·1°–95·8°/12 mm., 102·5°/17 mm., 104°–105°/23 mm., or 170°/250 mm.; sp.gr. 1·16817 at 20°/4°, 1·856 at 4°/4°, 1·1753 at 11°·15°, 1·1674 at 15°/15°; and yields the *anhydride*, m.p. 72·5°, on heating with oxalic acid (Anschütz and Berns, Ber. 1887, 20, 1389; Schott, *ibid.*

1896, 29, 1986; Perkin, Chem. Soc. Trans. 1896, 69, 1244).

Phenylacetamide $C_6H_5 \cdot CH_2 \cdot CO \cdot NH_2$ has m.p. 154°–155°, b.p. 281°–284° (Weddige, J. pr. Chem. 1873, [ii.] 7, 100); the *diethylamide* has m.p. 86°, b.p. 295°–297° (corr.); the *diphenylamide* has m.p. 72° (Hausknecht, Ber. 1889, 22, 324); the *hydrazide* has m.p. 116°; the *aziomide* is a colourless oil and yields with bromine a crystalline compound, m.p. 121° (Boetzelen, J. pr. Chem. 1901, [ii.] 64, 314). *Phenylaceturonitrile* $C_6H_5 \cdot CH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CN$ has m.p. 90·5°; *ethyl phenylaceturate*, m.p. 82° (Klages and Haack, Ber. 1903, 36, 1646); *phenylacetylurethane*, m.p. 113° (Diels, *ibid.* 1903, 36, 736).

Phenylacetic acid and the derivatives described above contain a methylene group of similar reactivity to that in malonic acid, ethyl acetoacetate, &c., and they therefore undergo the Claisen condensation (Boëseken, Rec. trav. chim. 1896, 15, 161; Hodgkinson, Chem. Soc. Proc. 1886, 188); form condensation products with aldehydes (Röhmer, Ber. 1898, 31, 281; Boetzelen, J. pr. Chem. 1901, [ii.] 64, 314); react with ethyl nitrate and nitrite (Müller, Ber. 1883, 16, 1617, 2985; Wislicenus and Grützner, *ibid.* 1909, 42, 1930; Noelting and Kadiera, *ibid.* 1906, 39, 2056); and form halogen substituted and amino derivatives that contain an asymmetric carbon atom and have been resolved into their optically active constituents (Easterfield, Chem. Soc. Trans. 1891, 71; Walden, Ber. 1895, 28, 1287; Zeitsch. physikal. Chem. 1895, 17, 705; Bischoff, Ber. 1897, 30, 276; Kossel, *ibid.* 1891, 24, 4145; Stadnikoff, J. Russ. Phys. Chem. Soc. 1906, 38, 943; Ehrlich and Wendel, Biochem. Zeitsch. 1908, 8, 438 Fischer and Weichhold, Ber. 1908, 41, 1286; Betti and Mayer, *ibid.* 2071).

In addition to the derivatives already described or to which reference has been made, phenylacetic acid forms a series of substituted derivatives in which the substituent has replaced hydrogen of the benzene ring. With the exception of a *dihydroxy* derivative (*homogentisic acid*), the compounds belonging to this series are not of sufficient importance for the purpose of this article to merit a detailed description; and for the preparation and properties of the halogen, nitro and nitro-halogen, &c., derivatives, *see* Jackson and Lowery, Ber. 1877, 10, 1209; Jackson and Field, Amer. Chem. J. 2, 85; Mabery and Jackson, Ber. 1878, 11, 55; Zincke and Böttcher, Annalen, 1905, 343, 100; Maxwell, Ber. 1879, 12, 1764; Bedson, Chem. Soc. Trans. 1880, 90; Gabriel, Ber. 1881, 14, 2341; 1882, 15, 834, 1992; Gabriel and Meyer, *ibid.* 1881, 14, 823; Gabriel and Borgmann, *ibid.* 1883, 16, 2064; Meyer, Chem. Zentr. 1885, 516; Ber. 1888, 21, 1306; Bedson, *ibid.* 1877, 10, 530, 1657; Jackson and Robinson, Amer. Chem. J. 11, 541; Jackson and Carlton, *ibid.* 1904, 31, 360; Jackson and Shortt Smith, *ibid.* 1904, 32, 168; Reissert, Ber. 1908, 41, 3921; Traube, *ibid.* 1882, 15, 2110; and Mellinghoff, *ibid.* 1889, 22, 3207; Borsche and Bahr, Annalen, 1913, 402, 81; Jacobs & Heidelberger, J. Amer. Chem. Soc. 1917, 39, 1439; Lyman and Reid, *ibid.* 1917, 39, 701; Pyman, Chem. Soc. Trans. 1917, 111, 169; Bloch, Zeitsch. physiol. Chem. 1917, 100, 226; Borsche, Slackmann and Makaroff-Semljanski, Ber. 1916, 49, 2222; Jacobs, Heidelberger and Rolf, J. Amer. Chem. Soc. 1919, 41, 458).

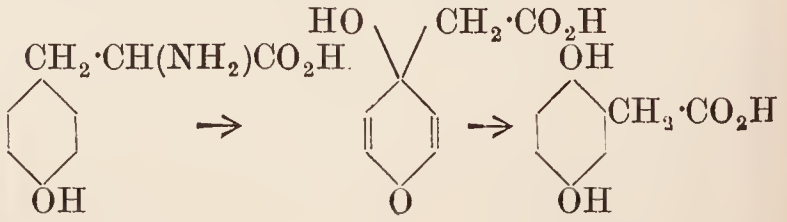
Homogentisic acid, 2 : 5-*dihydroxyphenylacetic acid, quinolacetic acid*

$$C_6H_3(OH)_2CH_2 \cdot CO_2H$$

occurs in the urine of certain individuals suffering from *alcaptonuria*, the name *alcapton* being applied by Bödeker (Zeit. rat. Med. 1859, 7, 130) to a reducing substance occurring in certain urines that became brown on addition of alkali in the presence of oxygen (*compare* also Kirk, Brit. Med. J. 1888, 2, 232; 1889, 2, 1149). The acid was first isolated and identified by Wolkow and Baumann (Zeitsch. physiol. Chem. 1894, 15, 228), and the name *homogentisic acid* applied to it. Homogentisic acid occurs also in the blood serum of alcaptonurics (Abderhalden and Falta, Zeitsch. physiol. Chem. 1903, 39, 143); but the statements that it is found in sugar-beet juice (Gonnermann, Chem. Zeit. 1899, 23, 213) and in seedlings (Bertel, Chem. Zentr. 1903, i. 178) have not been confirmed by later investigations (Schulze, Zeitsch. physiol. Chem. 1907, 50, 508; Schulze and Castoro, *ibid.* 1906, 48, 396).

Origin of homogentisic acid in the organism. According to Embden (Zeitsch. physiol. Chem. 1895, 17, 182; 18, 304); Wolkow and Baumann, (*l.c.*); Mittelbach (Chem. Zentr. 1901, ii. 1213); Neubauer and Falta (Zeitsch. physiol. Chem. 1904, 42, 81); Blum (Arch. exp. Path. Pharm. 1908, 59, 273); and Neubauer (Deut. Archiv. Klin. Med. 1909, 95, 211), homogentisic acid is a degradation product of phenylalanine and tyrosine, and in the normal individual it undergoes ultimate oxidation to carbon dioxide and water, but owing to an idiosyncrasy in metabolism the alcaptonuric excretes the acid without further change. Normal sera of man contain a ferment which is capable of destroying homogentisic acid. This ferment is absent in the sera of alcaptonurics (Gross, Biochem. Zeitsch. 1914, 61, 165). Dakin and Wakeman (J. Biol. Chem. 1911, 9, 139, 151), however, maintain that alcaptonuria represents a condition in which the formation of homogentisic acid is abnormal as well as the failure to effect its katabolism when formed, for such individuals have not lost their power to katabolise simple derivatives of phenylalanine and tyrosine (*e.g.* *p*-methylphenylalanine or *p*-methoxyphenylalanine) provided their structure is such that the formation of substances of the type of homogentisic acid is excluded.

The mechanism of the change whereby tyrosine is converted into homogentisic acid is somewhat obscure. According to Blum, *l.c.*, Friedmann (Beitr. Chem. Physiol. Path. 1908, 11, 304), Neubauer, *l.c.*, Suwa (Zeitsch. physiol. Chem. 1911, 72, 113), the side chain is first degraded, then a relative change of position of the side chain and the hydroxyl group, and a secondary oxidation take place concurrently



Tyrosine. Homogentisic acid

The average excretion of homogentisic acid in cases of alcaptonuria is fairly uniform (Garrod and Hele, J. Physiol. 1905, 33, 198); the amount is, however, increased by the administration of tyrosine or phenylalanine, or of peptides or proteids that yield tyrosine on hydrolysis (Embden, Zeitsch. physiol. Chem. 1895, 17, 182; 18, 304; Falta and Langstein, *ibid.* 1903, 37, 513; Neubauer and Falta, *ibid.* 1904, 42, 81; Abderhalden and Bloch, *ibid.* 1907, 52, 435; 53, 464; Abderhalden, Massini, *ibid.* 1910, 66, 140; Blum, *l.c.*; Neubauer, *l.c.*; Abderhalden, *ibid.* 1912, 77, 454).

Homogentisic acid has been synthesised by heating quinol dimethyl ether dissolved in carbon disulphide with ethylchloracetate and aluminium chloride, and subsequent hydrolysis with red phosphorus and fuming hydriodic acid of the methyl ether of homogentisic acid thus obtained (Osborne, Proc. Physiol. Soc. 1903, 13, 14).

Homogentisic acid forms prisms that melt at 146·5°–147°, and pass into the *lactone*

$$OH\cdot C_6H_3\langle \begin{matrix} O- \\ CH_2 \end{matrix} \rangle CO,$$

m.p. 191°. The *lead salt* $Pb(C_8H_7O_4)_2,3H_2O$ has m.p. 214°–215°, is soluble in 675 parts of water at 20°, and advantage is taken of this sparing solubility in the isolation of the acid. The *ethyl ester* has m.p. 119°–120°; the *dimethyl ester* $(OMe)_2C_6H_3\cdot CH_2\cdot CO_2H$ has m.p. 124·5°; and its *methyl ester* $(OMe)_2C_6H_3\cdot CH_2\cdot CO_2Me$, m.p. 45° (Wolkow and Baumann, Zeitsch. physiol. Chem. 1894, 15, 228; Baumann and Fränkl, *ibid.* 20, 221). *Dibenzoylhomogentisamide* has m.p. 204° (Orton and Garrod, J. Physiol. 1901, 27, 89). Homogentisic acid reduces copper and silver salts readily, gives a blue colour with ferric chloride, and yields gentisic acid (2 : 5-dihydroxybenzoic acid) and quinol on fusion with potassium hydroxide at 196°–198°. For the chemistry of the colour reactions afforded by homogentisic acid with amines, *see* Mörner, Zeitsch. physiol. Chem. 1910, 69, 329.

Estimation.—Homogentisic acid in urine is estimated by measuring its reducing action on silver nitrate. 10 c.c. of the filtered urine, 10 c.c. of ammonia solution (8 p.c.), 20 c.c. of N/10 silver nitrate solution are placed in a flask; after five minutes 5 drops of calcium chloride and 10 drops of ammonium carbonate solution are added, the solution made up to 50 c.c., and the silver estimated in half the filtrate. One molecule of homogentisic acid reduces 4 atoms of silver (Baumann, Zeitsch. physiol. Chem. 1895, 16, 268; Denigés, J. Pharm. Chem. 1897, [vi.] 5, 50; Garrod and Hurtley, J. Physiol. 1905, 33, 206; Mutch, *ibid.* 49, ii.–iii.). M. A. W.

PHENYLALANINE, *β-phenyl-α-aminopropionic acid, α-aminohydrocinnamic acid*

$$C_6H_5\cdot CH_2\cdot CH(NH_2)CO_2H$$

was discovered in the etiolated seedlings of *Lupinus luteus* (Schulze and Barbieri, Ber. 1879, 12, 1924; 1881, 14, 1785), and occurs in many other germinating plants (Schulze, Zeitsch. physiol. Chem. 1888, 12, 405; 1892, 17, 193; 1894, 20, 306; 1896, 22, 411; 1900, 30, 241). Winterstein (*ibid.* 1904, 41, 485) found it among other products of proteid hydrolysis in Emmenthaler cheese; and Abderhalden and Barker (*ibid.* 1904, 42, 524) showed that it occurs in the urine of dogs suffering from phosphorus poisoning.

The naturally occurring phenylalanine (*l*-phenylalanine) originates from the protein of the germinating plant, and it can also be readily obtained by the hydrolysis of a large number of proteids (*v.* PROTEINS) by means of hydrochloric acid, stannous chloride, or baryta (Schulze and Barbieri, Ber. 1883, 16, 1711; Zeitsch. physiol. Chem. 1884, 9, 63); it occurs in that fraction of the esterified products of hydrolysis that boils at 130°–160°/0·5 mm., and is isolated by precipitation from the mixed esters by means of water (Fischer, *ibid.* 1901, 33, 412), or by means of its sparingly soluble copper salt (Schulze and Barbieri, J. pr. Chem. 1883, [ii.] 27, 337; *compare* Schulze and Winterstein, Ber. 1902, 35, 210). For the separation of phenylalanine from, and its estimation in, the products of hydrolysis of proteins, *see* Kodama (J. Tokyo Chem. Soc. 1920, 41, 479).

An orange coloration is obtained when a solution of phenylalanine in concentrated sulphuric acid is heated with a drop of formaldehyde solution, the colour changing rapidly to brown. When a solution of phenylalanine in sulphuric acid is mixed with a drop of paracetaldehyde, in 90 p.c. alcohol, a lemon-yellow coloration develops within about ten minutes; the colour increases in intensity and, after an hour, exhibits a green fluorescence (Chelle, Ann. Chim. anal. 1914, 19, 109). According to Chelle this reaction may be used for a colorimetric estimation of phenylalanine.

Synthesis.—The constitution of phenylalanine was determined by Erlenmeyer and Lipp (Ber. 1882, 15, 1006), who synthesised it from phenylacetaldehyde, hydrogen cyanide, and ammonia

$$C_6H_5\cdot CH_2\cdot CHO \rightarrow C_6H_5\cdot CH_2\cdot CH(NH_2)CN \rightarrow C_6H_5\cdot CH_2\cdot CH(NH_2)CO_2H$$

Plöchl (*ibid.* 1883, 16, 2815; 1884, 17, 1616) obtained it by the reduction and subsequent hydrolysis of α-benzoylaminocinnamic acid obtained by the condensation of benzaldehyde with hippuric acid in the presence of acetic anhydride—

$$C_6H_5\cdot CHO + CH_2(NH\cdot COPh)CO_2H \rightarrow C_6H_5\cdot CH : C(NH\cdot COPh)CO_2H \rightarrow C_6H_5\cdot CH_2\cdot CH(NH\cdot COPh)CO_2H \rightarrow C_6H_5\cdot CH_2\cdot CH(NH_2)CO_2H.$$

For a complete explanation of the mechanism of this reaction which is more complex than indicated above, *see* Erlenmeyer (Annalen, 1893, 275, 1, 13); and Erlenmeyer and Kunlin (*ibid.* 1899, 307, 146).

For the preparation of synthetic phenylalanine Fischer's method is the most practical (Ber. 1904, 37, 3062). It consists in the preparation of the corresponding bromo-fatty acid starting with ethyl malonate and benzyl chloride, and treating this with ammonia—

$$(CO_2Et)_2CH_2 \rightarrow (CO_2Et)_2CH\cdot CH_2\cdot C_6H_5 \rightarrow (CO_2H)_2CH\cdot CH_2\cdot C_6H_5 \rightarrow (CO_2H)_2CBr\cdot CH_2\cdot C_6H_5 \rightarrow CO_2H\cdot CHBr\cdot CH_2\cdot C_6H_5 \rightarrow CO_2H\cdot CH(NH_2)CH_2\cdot C_6H_5$$

For other methods of synthesis, *see* Sörensen (Zeitsch. physiol. Chem. 1905, 44, 448); Wheeler

and Hoffman (Amer. Chem. J. 1911, 45, 368; Johnson and O'Brien, J. Biol. Chem. 1912, 12, 203).

The phenylalanine obtained by any of the synthetic processes described above is the racemic (*dl*-) form, it can be resolved into its optically active isomerides by the fractional crystallisation of the cinchonine salt of the benzoyl derivative (Fischer and Mouneyrat, Ber. 1900, 33, 2383), the brucine salt of the formyl derivative (Fischer and Schoeller, Annalen, 1907, 357, 1), or the strychnine salt of β-phenyl-α-carbamido-propionic acid, obtained by the action of potassium cyanate on phenylalanine (Dakin and Dudley, J. Biol. Chem. 1914, 17, 29). *d*-Phenylalanine can be obtained by the selective action of yeast in a sucrose solution on *dl*-phenylalanine (Ehrlich, Biochem. Zeitsch. 1908, 8, 438). *Bacillus protius* attacks *l*-phenylalanine whilst *B. subtilis* attacks both antipodes. Each organism forms phenyl lactic acid and phenylethylamine, Amatsu and Tsudji (Acta Scholae Med. Univ. Imperial Kioto, 1918, 2, 447).

l-**Phenylalanine** crystallises in anhydrous shining plates or hydrated needles containing 4 p.c. water (Schulze and Winterstein, *l.c.*), soluble in 32·4 parts of water at 25°, m.p. 278° corr.) with decomposition, $[\alpha]_D^{20}-35{\cdot}1°$, and has a slightly bitter taste (Fischer and Schoeller, *l.c.*). The *copper salt* $(C_9H_{10}O_2N)_2Cu$ is almost insoluble in water; the *hydrochloride*

$$C_9H_{11}O_2N,HCl$$

and *hydrobromide* are crystalline and stable; the *ethyl ester* $C_8H_{10}N{\cdot}CO_2Et$ is an oil and forms a crystalline *hydrochloride* $C_8H_{10}N{\cdot}CO_2Et,HCl$, $[\alpha]_D^{20}-7{\cdot}6°$; the *formyl* derivative forms sharp four-sided plates, m.p. 167° (corr.), and has $[\alpha]_D^{20}+75{\cdot}2°$; the *brucine* salt crystallises in warty masses from methyl alcohol; the *benzoyl* derivative is more readily soluble than that of the racemic form, and has not been obtained pure (Fischer, Mouneyrat, Schoeller, *l.c.*). *p-Toluenesulphonyl-l-phenylalanine* has $[\alpha]_D^{20}$ $-2{\cdot}12°$ in acetone (Fischer and Lipschitz (Ber. 1915, 48, 360).

Physiological action. In the normal individual *l*-phenylalanine is completely destroyed in the system, and when administered as a food it causes no increase in the amount of aromatic substances in the urine; in certain abnormal cases (*alcaptonuria*) the phenylalanine is not completely oxidised in the system and is excreted in the form of homogentisic acid (*v.* PHENYLACETIC ACID); for its degradation in the organism *v.* Embden and Baldes (Biochem. Zeitsch. 1913, 55, 301).

d-**Phenylalanine** forms beautiful plates soluble in 35·2 parts of water at 16°, m.p. 283°–284° (corr.), with decomposition; $[\alpha]_D^{16°}+35{\cdot}08°$ in 2 p.c. aqueous solution; $[\alpha]_D^{20°}+7{\cdot}07$ in 3·5 p.c. solution of 18 p.c. hydrochloric acid (Fischer and Mouneyrat, *l.c.*); and has a sweet taste. The *hydrobromide* forms silky needles, the *formyl* derivative $C_{10}H_{11}O_3N$ crystallises in needles or plates $[\alpha]_D^{20}-75{\cdot}43°$, soluble in 145 parts of water at 27°, and melts at 167° (corr.); the *benzoyl* derivative $C_{16}H_{15}O_3N$ forms colourless needles, m.p. 145°–146° (corr.), $[\alpha]_D^{20}-17{\cdot}1°$ in 7 p.c. N/1 alkali solution, the *cinchonine salt* melts at 180°–181°; the *phenyl*isocyanate $C_{16}H_{16}O_3N_2$ has m.p. 180°–181° (corr.), $[\alpha]_D^{20°}+61{\cdot}27°$ in 8 p.c. alkali solution; the *α-naphthyl*isocyanate $C_{20}H_{18}O_3N_2$ has m.p. 150°–151° (Neuberg and Rosenberg, Biochem. Zeitsch. 1907, 5, 458). *p-Toluenesulphonyl-d-phenylalanine*, $CH_2Ph{\cdot}CH(NH{\cdot}SO_2{\cdot}C_7H_7)COOH$, m.p. 164°–165° (corr.), has $[\alpha]_D^{19}+2{\cdot}42$ (in acetone); *d*-N-*phenylmethylalanine* crystallises in colourless needles and has $[\alpha]_D^{18}-48{\cdot}22°$ in N/10 sodium hydroxide and $[\alpha]_D^{20}-17{\cdot}7°$ in N-hydrochloric acid (Fischer and Lipschitz, *l.c.*).

dl-**Phenylalanine** crystallises from water in short stunted prisms, from alcohol in shining plates, difficultly soluble in cold water; it melts at 263°–265° with decomposition (Erlenmeyer and Lipp, *l.c.*), or at 271°–273° (Sörensen, *l.c.*). The acidic dissociation constant is $2{\cdot}5\times10^{-9}$ and the basic dissociation constant is $1{\cdot}3\times10^{-12}$ (Kanitz, Pflüger's Archiv. 1907, 118, 537). The behaviour of phenylalanine on heating is characteristic, a small quantity sublimes unchanged (1·5 grms. yielded 0·06 grm. sublimate after $2\frac{1}{2}$ hours at 200°/1·5–2 mm., Dakin, J. Biol. Chem. 1909, 6, 235), the remainder decomposes with evolution of carbon dioxide and water and formation of a residue of *phenyllactimide* (*v. infra*), and a distillate of *phenylethylamine* (Schulze and Barbieri, *l.c.*; Erlenmeyer and Lipp, *l.c.*). On oxidation with chromic acid mixture phenylalanine yields phenylacetaldehyde and finally benzoic acid.

In its physiological action *dl*-phenylalanine resembles the *l*-form, being completely oxidised in the organism of the normal individual, and converted into homogentisic acid in the cases of alcaptonuria, although the conversion of racemic phenylalanine is less complete than that of the *l*- form (Falta and Langstein, Zeitsch. physiol. Chem. 1903, 37, 513). After intravenous or subcutaneous injection of *dl*-phenylalanine in cats or dogs, a large amount is excreted unchanged, and part is converted into α-carbamido-β-phenylpropionic acid (Dakin, J. biol. Chem. 1909, 6, 203), for the identification of this acid in urine, *see* Rohde (J. Biol. Chem. 1917, 29).

Derivatives of dl-*phenylalanine.* The *hydrochloride* $C_9H_{11}O_2N{\cdot}HCl$, the *platinichloride*

$$(C_9H_{11}O_2N)_2{\cdot}H_2PtCl_6$$

the *nitrate* $C_9H_{11}O_2N{\cdot}HNO_3$, the *sulphate* $(C_9H_{11}O_2N)_2H_2SO_4$, the *picrate*

$$(C_9H_{11}O_2N)_2C_6H_3O_7N_3$$

m.p. 173°, and *picrolonate* $C_9H_{11}O_2N{\cdot}C_{10}H_8O_5N_4$, m.p. 238°, are crystalline. The *copper* salt

$$(C_9H_{10}O_2N)_2Cu,2H_2O$$

is sparingly soluble in cold water, and becomes anhydrous over sulphuric acid; the *silver salt* $C_9H_{10}O_2NAg$ is sparingly soluble. The *ethyl ester* $C_8H_{10}N{\cdot}CO_2Et$ is a thick oil sparingly soluble in water, b.p. 143°/10 mm., sp.gr. 1·065 at 15°, forms a crystalline *picrate*, m.p. 156·5° (corr.), *hydrochloride* $C_8H_{10}N{\cdot}CO_2Et,HCl$, m.p. 127°, *nitrite* $C_8H_{10}N{\cdot}CO_2Et{\cdot}HNO_2$, and a *diazo derivative* (ethyl α-diazo-β-phenylpropionate)

$$C_6H_5{\cdot}CH_2{\cdot}C(N_2)CO_2Et$$

a golden-yellow oil, b.p. 90°–94°/11 mm., sp.gr. 1·107 at 10°/4°, n_D 1·5367 at 16° (Curtius and Müller, Ber. 1904, 37, 1261). The *methyl ester* $C_8H_{10}N{\cdot}CO_2Me$ has b.p. 141°/12 mm., sp.gr. 1·096 at 22°/4°, n_D 1·5203 at 20°; the *hydrochloride* has m.p. 158°; the *diazo derivative* $C_6H_5{\cdot}CH_2{\cdot}C(N_2)CO_2Me$, bright orange-coloured liquid, b.p. 85°–87°/12 mm., sp.gr. 1·126 at 20°/4°, n_D 1·5435 at 26° (Curtius and Müller, *l.c.*).

dl-*α*-*Amino*-*β*-*phenylpropionalacetal*

$$C_6H_5{\cdot}CH_2{\cdot}CH(NH_2)CH(OEt)_2$$

obtained by reducing the ethyl ester, has b.p. 103°–105° (corr.), 0·25 mm. or 153·5°/11 mm., sp.gr. 0·995 at 20°; n_D 1·49383 (Fischer and Kametaka, Annalen, 1909, 365, 7). The *hydrochloride* of dl-*phenylalaninechloride*

$$C_6H_5{\cdot}CH_2{\cdot}CH(NH_2{\cdot}HCl)COCl$$

is a colourless powder; the *amide*

$$C_6H_5{\cdot}CH_2{\cdot}CH(NH_2)CONH_2$$

has m.p. 138°–139° (corr.), and yields the *β*-*naphthalenesulphonyl* derivative $C_{19}H_{18}O_3N_2S_2$, m.p. 164°–166° (corr.), and *carbethoxy*-dl-*phenylalanineamide*, m.p 141° (corr.), and with oxalyl chloride gives 2 : 3 : 6-*triketo*-5-*benzylpiperazine*

$$CH_2Ph{\cdot}CH\begin{matrix}CO{\cdot}NH\\NH{\cdot}CO\end{matrix}>CO$$

m.p. 170° (Koenigs and Mylo, Ber. 1908, 41, 4427; Bornwater, Rec. trav. chim. 1917, 36, 250). *Formyl*-dl-*phenylalanine* $C_{10}H_{11}O_3N$ is soluble in 240 parts of water at 27°; the *benzoyl* derivative $C_{16}H_{15}O_3N$ has m.p. 187°–188° (corr.) (Fischer and Mouneyrat), its *methyl ester* $C_{16}H_{14}O_3N{\cdot}CH_3$ melts at 87° (corr.), and its *ethyl ester* at 95° (corr.), the *acid chloride* $C_{15}H_{14}ON{\cdot}COCl$ has m.p. 123°–125° with decomposition, and the *amide* $C_{15}H_{14}ON{\cdot}CONH_2$ melts at 198° (corr.) (Max, Annalen, 1909, 369, 276). *Phenacetyl*-dl-*phenylalanine*

$$C_6H_5{\cdot}CH_2{\cdot}CH(NH{\cdot}CO{\cdot}CH_2Ph)CO_2H$$

m.p. 126° (Erlenmeyer and Kunlin, *l.c.*). *Phenyllactimide* (3 : 6 - *dibenzyl* - 2 : 5-*diketopiperazine*)

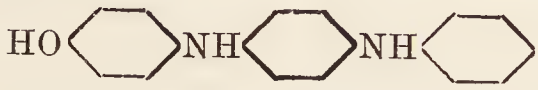
$$C_6H_5{\cdot}CH_2{\cdot}CH\begin{matrix}NH{\cdot}CO\\CO{\cdot}NH\end{matrix}>CH{\cdot}CH_2{\cdot}C_6H_5$$

has m.p. 300° (corr.) (Erlenmeyer and Lipp, *l.c.*; Curtius and Müller, *l.c.*).

*Phenyl*isocyanate of dl-*phenylalanine* has m.p. 182° (with decomp.); the *methyl*isocyanate has m.p. 176°–177°, $[\alpha]_D$ −14° 8′ (Vallée, Ann. Chim. 1908, [viii.] 15, 331); *Di-hydroxyphenylalanine* $C_6H_3(OH)_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$ (*α*-amino-*β*-3 : 4-dihydroxyphenyl propionic acid), crystallises in stunted prisms or slender needles, m.p. 280° (decomp.), and has $[\alpha]_D^{20}$ −14·28°; it is identical with the nitrogenous substance observed by Torquati (Arch. Farm. Sperm. 1913, 15, 213) in the seedlings of *Vicia faba*. The 2 : 5 : 6-*tri*-bromo derivative has m.p. 200° (decomp.). Guggenheim (Zeitsch. physiol. Chem. 1913, 88, 276). The inactive form of the acid, m.p. 263°–270°, has been synthesised by Funk (Chem. Soc. Trans. 1911, 99, 554) and by Stephen and Weizmann (*ibid.* 1914, 105, 1152).

For a description of the preparation and properties of the chloro, bromo, iodo, nitro, and amino substituted derivatives of phenylalanine in which the substituent is in the benzene ring, *see* Wheeler and Clapp, Amer. Chem. J. 1908, 40, 337, 458; Abderhalden and Brossa, Ber. 1909, 42, 3411; Erlenmeyer and Lipp, *l.c.*; Friedmann and Maase, Biochem. Zeitsch. 1910, 27, 97; Flatow, Zeitsch. physiol. Chem. 1910, 64, 367. Numerous *polypeptides* containing the phenylalanyl radicle are described by Leuchs and Suzuki (Ber. 1904, 37, 3306); Curtius and Müller (J. pr. Chem. 1904, [ii.] 70, 223); Fischer (Ber. 1904, 37, 3062); Fischer and Blank (Annalen, 1907, 354, 1); Fischer and Schoeller (*ibid.* 1907, 357, 1); Abderhalden and Brossa (Ber. 1909, 42, 3411). M. A. W.

4-PHENYLAMINO-4′-HYDROXYDIPHENYLAMINE



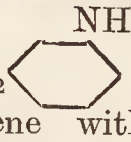
Prepared by oxidising a mixture of *p*-amino diphenylamine and phenol or a mixture of diphenylamine and *p*-aminophenol (Cassella & Co. D. R. P. 150553; Eng. Pat. 16823 of 1902). Readily soluble in alcohol; sparingly soluble in water.

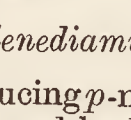
PHENYLBARBITAL. Syn. for luminal.

PHENYLBENZYLHYDRAZINE *v.* HYDRAZINES.

PHENYLENE BLUE *v.* INDAMINES AND INDOPHENOLS.

PHENYLENE BROWN *v.* AZO- COLOURING MATTERS.

PHENYLENEDIAMINES. *m-Phenylenediamine*  is made by reducing *m*-dinitrobenzene with iron and hydrochloric acid, adding sodium carbonate, filtering, the solution evaporated and mixed with hydrochloric acid (*cf.* Grandmougin, Rev. prod. chim. 1917, 20, 260; Pomeranz, D. R. P. 269542). M.p. 61°, b.p. 282°–284°. Readily soluble in water. Used in making azo-dyes.

p-Phenylenediamine  . Prepared by reducing *p*-nitroaniline or aminoazo-benzene by iron and hydrochloric acid. For details of manufacture, *see* Jansen (Zeitsch. Farb. Ind. 1913, 12, 197; also Cain's Intermediate Products for Dyes). May also be prepared by reduction with hydrogen, using nickel as a catalyst, in amyl alcoholic solution, at 120°–130° under a pressure of 10–15 kilos. per sq. cm. (Brochet, Eng. Pat. 16936 of 1913), m.p. 147°; b.p. 267°. Used as a hair dye and in the manufacture of safranine and sulphide dyes. According to Callan and Henderson (J. Soc. Chem. Ind. 1919, 38, 408T), *p*-phenylenediamine may be estimated by adding it to a solution of sodium hypochlorite containing sodium carbonate, the amount of hypochlorite (or available chlorine) removed from the solution is proportionate to the amount of *p*-phenylenediamine present

$$C_6H_4(NH_2)_2+6Cl=C_6H_4(NCl)_2+4HCl$$

the amount of available chlorine so removed being determined by standard sodium arsenite solution.

o-PHENYLENE DIAZO SULPHIDE *v.* DIAZO COMPOUNDS.

PHENYLENE VIOLET *v.* INDAMINES AND INDOPHENOLS.

PHENYLGLYCINE. This compound and certain of its derivatives, more especially phenylglycine nitrile, phenylglycine-*o*-carboxylic acid and its nitrile, have during the last few decades assumed great technical importance, owing to the fact that they are all intermediate products in the manufacture of indigo by one or other of the processes based on the original synthetic method of Heumann (*cf.* INDIGO, ARTIFICIAL).

Phenylglycine, anilinoacetic acid

$$C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}COOH$$

may be obtained by the action of aniline on chloroacetic or bromoacetic acid (Hausdörfer, Ber. 1899, 22, 1799). The yields, however, are bad, owing to the fact that there is a tendency for two molecules of acid to condense with one of aniline. To avoid this a salt or ester of chloroacetic acid may be employed; various other processes have also been suggested.

Technical methods of preparation.

(1) Aniline is made to condense with an alkali or alkaline earth salt of chloroacetic acid (Friswell, Eng. Pat. 18149, 1907; D. R. P. 177491). The condensation is brought about in the presence of hydrated ferrous oxide or carbonate (Höchster Farbw. D. R. P. 167698). An ingenious modification of this process is to heat an aqueous solution of chloroacetic acid with nitro-benzene in the presence of finely divided iron, which first brings about the reduction of the nitro-benzene and then forms the insoluble iron salt of phenylglycine. In actual practice it is found advisable to add a small quantity of aniline to start the reaction, which takes place at 100°. When the change is complete, the mixture is distilled with steam to remove the unchanged aniline, and excess of sodium carbonate is added. The solution of the sodium salt of phenylglycine is then filtered and the phenylglycine precipitated by the addition of sulphuric acid (Höchster Farbw. D. R. P. 115797; Eng. Pat. 9700, 1906).

Amyl chloroacetate may be employed instead of the free acid to condense with aniline, and the resulting amyl ester is then saponified (Leppmann, D. R. P. 163515).

(2) Phenylglycine may also be prepared by the reduction of oxanilic acid

$$C_6H_5{\cdot}NH{\cdot}CO{\cdot}COOH$$

which may be obtained in good yields by heating aniline with excess of oxalic acid. Two methods have been proposed (1) by reduction with sodium amalgam or with zinc-dust (Köpp & Co., D. R. P. 163842); (2) by electrolytic reduction with lead cathodes (Kinzlberger, D. R. PP. 163842, 210693).

(3) Phenylglycine is now prepared in large quantities by the saponification of its nitrile, $C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}CN$, which may be obtained from aniline in good yields by the action of prussic acid and formaldehyde (D. R. P. 145376).

Properties and Reactions.—White crystals, m.p. 127°, moderately soluble in water, slightly so in ether, but easily so in the usual organic solvents. It forms soluble alkali salts and a green insoluble copper salt, which is an internal complex. On heating, it loses at 140° a molecule of water; on fusion with alkalis it loses water, forming indoxyl, which on oxidation in the air yields indigo; with fuming sulphuric acid it forms indigo sulphonic acid; with bromine water its aqueous solution gives a precipitate of tribromophenylglycine; with acetic anhydride it forms acetylphenylglycine.

The conversion of Phenylglycine into Indigo.—The fusion with soda or potash to form indoxyl and the subsequent oxidation of this compound by atmospheric oxygen requires a temperature of over 300°, and the yields of indigo are extremely unsatisfactory; it was this fact which made the original Heumann synthesis commercially impracticable. Various condensing agents have been since proposed, and now sodamide is employed extensively and with considerable technical success, in spite of the expense of the sodamide, in the Höchster dye works.

Among other substances which have been suggested are sodium oxide mixed with soda (Basler Chemische Fabrik, D. R. P. 165691), and also calcium carbide and magnesium nitride (Höchster Farbw., D. R. P. 166213).

Derivatives.—Phenylglycine methyl ester (m.p. 48°) and *ethyl ester* (m.p. 58°) from aniline and the corresponding ester of chloroacetic acid (D. R. P. 194884).

Phenylglycine amide (m.p. 133°) from aniline and chloroacetamide.

Phenylglycine nitrile (m.p. 43°) from aniline and chloroacetonitrile, and also by the action of prussic acid and formaldehyde on aniline (Bender). On saponification it yields phenylglycine quantitatively.

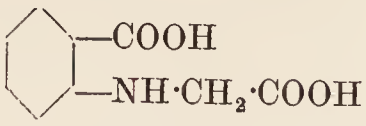
p-Hydroxyphenyglycine amide, from chloroacetamide and *p*-aminophenol, is employed as a photographic developer (D. R. P. 166799).

Nitro derivatives of phenylglycine are described by Deutsch (J. pr. Chem. 1907, [ii.] 76, 350); Borsche and Titsingh (Ber. 1907, 40, 5016); Reverdin (*ibid.* 1909, 42, 4115); Abderhalden and Blumberg (Zeitsch. physiol. Chem. 1910, 65, 318); Waldmann (J. pr. Chem. 1915, [ii.] 91, 190).

Phenylglycine-o-sulphonic acid, obtained by the action of formaldehyde and hydrogen cyanide on aniline-*o*-sulphonic acid (Bradshaw, Amer. Chem. J. 1906, 35, 340).

For a number of other derivatives of phenylglycine *see* Mauthner and Suida (Monatsh. 1890, 11, 380); Widman (Ber. 1896, 29, 1946); Fischer (*ibid.* 1899, 32, 247); Vorländer and Weissbrenner (*ibid.* 1900, 33, 555, 556); Kahn and Heimann (*ibid.* 1902, 35, 576); Schulz and Jockheim (*ibid.* 1908, 41, 3790); Leuchs and Geiger (*ibid.* 1721); Rupe and Vsétečha (Annalen, 1898, 301, 75); Rupe, Heberlien and Roesler (*ibid.* 79); Fischer and Schmidlin (*ibid.* 1905, 340, 190); Pickard (Chem. Soc. Trans. 1902, 1574); de Moulpied (*ibid.* 1905, 438); Lumière and Barbier (Bull. Soc. Chim. 1906, [ii.] 38, 123; Eng. Pat. 5763, 1900); Schlögl (J. pr. Chem. 1913, [ii.] 88, 251); Houben (Ber. 1913, 46, 3984); Poulenc Fréres and Oechslin (Fr. Pat. 473704); Meldola, Foster and Brightman (Chem. Soc. Trans. 1917, 111 552); Jacobs and Heidelberger (J. Amer. Chem. Soc. 1917, 39, 1447).

Phenylglycine-*o*-carboxylic acid



is an important intermediate product in the manufacture of indigo. It is obtained by the condensation of anthranilic acid and chloroacetic acid; as in the case of phenylglycine the yields are bad, but on working with the sodium salts in aqueous solution at a temperature of 40°, the reaction proceeds smoothly owing to the fact that the sodium salt of the acid crystallises out and is thus protected from further action. Various other methods have been suggested for the preparation of phenylglycine-*o*-carboxylic acid; by heating anthranilic acid or its salts with carbohydrates such as starch or mannite or with glycerol (Badische Anilin und Soda Fabrik, D. R. P. 111067); by heating glycine with *o*-chlorobenzoic acid in the presence of copper salts, which act as catalysts (Cie. Paris. Coul. d'Anilin, Fr. Pat. 306302); by the formation and subsequent saponification of ω-cyanomethylanthranilic acid (exonitrile of phenylglycine); by the action of formaldehyde and prussic acid on anthranilic acid (*cf.* phenylglycine nitrile). This method is used extensively, and is the subject of various patents (Farbw. Mühlhem, D. R. P. 117924; Badische Anilin und Soda Fabrik, D. R. P. 216748).

Properties and Reactions.—White crystals, m.p. 215° (decomp.); soluble in hot water, alcohol, ether, or acetic acid, but almost insoluble in benzene or chloroform. On heating with water it loses carbon dioxide and forms phenylglycine; on fusion with alkalis it first gives the salt of indoxylcarboxylic acid and then indoxyl, which in the presence of air is oxidised to indigo (Badische Anilin und Soda Fabrik, D. R. P. 111067); on heating with sodium acetate and acetic anhydride it forms diacetyl indoxyl (Bayer and Co., D. R. P. 85071); with fuming sulphuric acid it forms indigosulphonic acids.

Derivatives.—Phenylglycine-*o*-carboxylic acid being a dibasic acid, forms two series of mono esters, two nitriles, &c.

Dimethyl and diethyl esters, from the esters of chloroacetic acid and anthranilic acid (Höchster Farbw. D. R. P. 111911); also from the acid itself and alcohol (D. R. P. 120138).

Exonitrile (*v.* above).—Its acetyl derivative is obtained by the oxidation of acetyl-*o*-tolylglycine (Bayer and Co., D. R. P. 102892).

Halogen derivatives of phenylglycine-*o*-carboxylic acid are readily obtained by the action of halogens on the acid suspended in glacial acetic acid (D. R. PP. 148615, 158089, 216266; Friedländer, Bruckner and Deutsch, Annalen, 1912, 388, 23).

Nitro derivatives of the acid are described by Purgotti and Lunnine (Gazz. chim. ital. 1903, 33, [ii.] 324); Schwarz (Monatsh. 1905, 26, 1253). *Nitroso* derivatives, which are also used in the production of indigo, have been prepared by Vorländer (Ber. 1901, 34, 164; D. R. P. 127577); Riedel (D. R. P. 256461); Houben (Ber. 1913, 46, 3984).

Some other derivative of the acid and esters are described in D. R. PP. 138207, 141698, 147633; also by Lumière and Perrin (Bull. Soc. Chim. 1903, [iii.] 30, 966); Villiger (Ber. 1909, 42, 3541); also by Vorländer and Mumme (Ber. 1902, 35, 1699; D. R. PP. 216748; 220839).

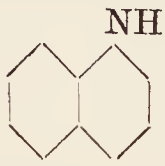
PHENYLHYDRAZINE *v.* HYDRAZINES.

PHENYLHYDRAZINE ACETYL *v.* PYRODINE.

PHENYLHYDRAZINE-*p*-SULPHONIC ACID *v.* HYDRAZINES.

PHENYLHYDRAZONES *v.* HYDRAZONES.

PHENYL-α-NAPHTHYLAMINE



Obtained by heating α-naphthol with aniline, or by heating α-naphthylamine with aniline and iodine under pressure at 230° and distilling the product *in vacuô* (Knoll and Co., D. R. P. 241853), m.p. 62°; b.p. 226°/15 mm.

1 - **PHENYLNAPHTHYLAMINE** - 8 - **SULPHONIC ACID.** Obtained by heating 1-naphthylamine-8-sulphonic acid with aniline and hydrochloric or benzoic acid (Fabr. vorm. F. Bayer and Co., D. R. P. 70349; Kalle and Co., D. R. P. 170630; Aktienges. f. Anilin, D. R. P. 158923). Sparingly soluble in water. Sodium salts very soluble.

PHENYL-*p*-PHENYLENEDIAMINE *v.* *p*-AMINODIPHENYLAMINE.

PHENYL HYDROGEN SULPHATE *v.* PHENOL AND ITS HOMOLOGUES.

PHENYLON (Methozin). A trade name for antipyrene.

PHENYLOSAZONES *v.* HYDRAZONES.

PHENYLPARACONIC ACID *v.* LACTONES.

PHENYLTHIOGLYCOL-*o*-CARBOXYLIC ACID  $S{\cdot}CH_2{\cdot}CO_2H$, m.p. 213°. Obtained by heating a solution of thiosalicylic acid in sodium hydroxide with chloroacetic acid and adding acid when phenylthioglycol-*o*-carboxylic acid is precipitated (Kalle and Co., D. R. P. 192075). Or the diazo compound obtained from anthranilic acid is heated in an alkaline solution with thioglycollic acid and the solution acidified; the precipitate is redissolved in a dilute solution of sodium carbonate and heated to the boiling-point; when nitrogen ceases to be evolved, the liquid is cooled and the phenylthio-*o*-carboxylic acid reprecipitated by hydrochloric acid; or a diazotised solution of anthranilic acid is mixed with a cooled solution of sodium sulphide containing sulphur. When the nitrogen is evolved, the solution is acidified and the precipitate is dissolved in a solution of sodium carbonate, filtered, and mixed with an alkaline solution of sodium chloroacetate, heated to 80°, filtered and the phenylthioglycol-*o*-carboxylic acid precipitated by acid (Kalle and Co., D. R. P 181658).

PHESIN. A sulpho derivative of phenacetin $C_6H_3(O{\cdot}C_2H_5)(SO_3Na)(NH{\cdot}CO{\cdot}CH_3)$ used as an antipyretic. Is a light-brown amorphous powder, soluble in water, giving a Bismarck brown solution (*v.* SYNTHETIC DRUGS).

PHILADELPHIA YELLOW G. *Chrysaniline* *v.* ACRIDINE DYESTUFFS.

PHILLIPSITE.[1] A mineral of the zeolite group of silicates with the approximate formula $R''Al_2(SiO_3)_4 \cdot 4H_2O$, where R″ is Ca and K_2, and less often Na_2, Ba, and Mg. Analyses show K_2O 2·66–10·93 p.c. The composition is, however, not constant, and F. Zambonini (1902) suggests the mixing of two silicates:

$$CaAl_2Si_2O_8 \cdot 4H_2O \text{ and } K_2Al_2Si_4O_{12} \cdot 4H_2O$$

Pseudophillipsite from Rome has the constant composition $R''_2Al_4Si_5O_{18} \cdot 9H_2O$. Crystals are monoclinic, but they always consist of two or more individuals with complex interpenetrating twinning and producing pseudo-orthorhombic, pseudo-tetragonal, and pseudo-cubic forms. They are quite small and often water-clear, glassy, and brilliant. The most usual form is that of square prisms with grooved edges. Small spherical groups with a radially fibrous structure and bristled with crystal-faces on the surface are not uncommon. Sp.gr. 2·2; H. $4\frac{1}{2}$. The mineral is readily decomposed by hydrochloric acid with separation of gelatinous silica. It is of common occurrence with other zeolitic minerals in the cavities of basic volcanic rocks, such as basalt, and more especially in those rich in alkalis, such as phonolite and leucitite. Well-known localities are Rome, Auvergne, northern Bohemia, &c. Crystals have been detected in the Roman masonry at the hot springs at Plombières and Bourbonne-les-Bains in France. Minute spherical aggregates have been found in the red clay on the floor of the deep ocean, the mineral having been formed here by the subaqueous alteration of volcanic debris. Phillipsite is the only zeolitic mineral that contains an appreciable amount of potassium, and very probably it plays an important part in the retention of potash in soils.

L. J. S.

PHLOGOPITE *v.* MICA.

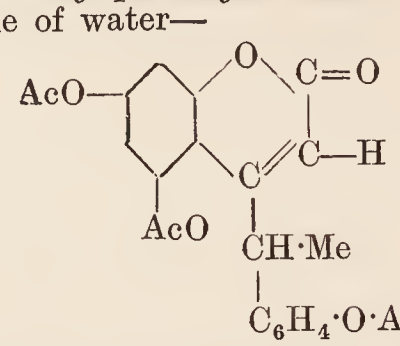
PHLORASPIN *v.* FILIXMAS.

PHLORETIN. Phloretin occurs in the form of two distinct glucosides, phloridzin and glycyphyllin, which are found in the root-bark of the apple, cherry, and plum-tree, and in the leaves of *Smilax glycyphylla* respectively (*cf.* Rennie, Jour Chem. Soc. 1887, 634); whilst by catalytic hydrogenation of naringenin, in alcoholic solution with palladous chloride and hydrogen, Franck (Beitr. Phys. 1, 179; *cf.* Chem. Zentr. 1914, ii. 253) obtained a dihydronaringenin which he considered to be identical with phloretin.

Mrs. H. A. Michael (Ber. 1894, 27, 2686), in consideration of the fact that by fusion with alkali phloretin yields phloroglucinol and phloretic acid, whilst on acetylation with acetic anhydride and sodium acetate a product was obtained which appeared to be a triacetyl derivative, proposed the formula

$$C_6H_3(OH)_2 \cdot O \cdot CO \cdot CH(Me) \cdot C_6H_4OH$$

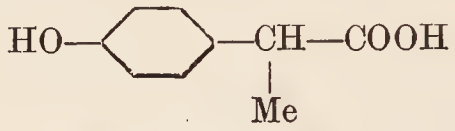
for phloretin. Ciamician and Silber (Ber. 1894, 27, 1627; 1895, 28, 1393), on further investigation of the product obtained by Michael, concluded that it was not a tri- but tetra-acetyl derivative, and found that when heated with excess of acetic anhydride and sodium acetate, it yielded *triacetyl-phloretyl-coumarin* by loss of one molecule of water—



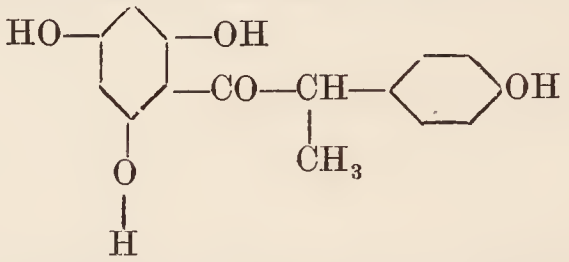
In this property the acetyl derivative of phloretin resembles the corresponding derivatives of maclurin and cotoïn. Ciamician and Silber, therefore, concluded that phloretin has the formula

$$C_6H_2(OH)_3 \cdot CO \cdot CH(Me) \cdot C_6H_4OH$$

They also obtained a trimethyl-ether and tetramethyl ether of phloretin in agreement with the above formula, and as phloretic acid has the structure



(Trinius, Annalen, 1885, 227, 262), that of phloretin may be represented thus—



E. Fischer and Nouri (Ber. 1917, 50, 611) have synthesised phloretin by the hydrolysis of the ketone-imide prepared by condensing acetyl phloretonitrile with phloroglucinol.

Phloretin $C_{15}H_{14}O_5$ crystallises in shining prisms, m.p. 250° (decomp.), almost insoluble in cold water, only sparingly in hot, but crystallises out on cooling. It is easily soluble in alcohol and may be crystallised from a mixture of alcohol and water; it is soluble in ether or hot glacial acetic acid. In caustic alkalis, or carbonates, it dissolves with yellow coloration, but is reprecipitated on acidification. If dissolved in concentrated aqueous ammonia, and the solution allowed to stand, golden-yellow scales are deposited. When boiled with concentrated aqueous potassium hydroxide for about fifteen minutes it is decomposed with formation of phloroglucinol and phloretic acid.

The *tetra-acetyl derivative* melts at 95°, and by loss of water when heated with acetic anhydride and sodium acetate, yields

Triacetyl-phloretyl-coumarin $C_{23}H_{20}O_8$ which melts at 173°, and from which *trihydroxy-phloretyl-coumarin* $C_{17}H_{14}O_5$, melting at 213°, may be obtained by hydrolysis.

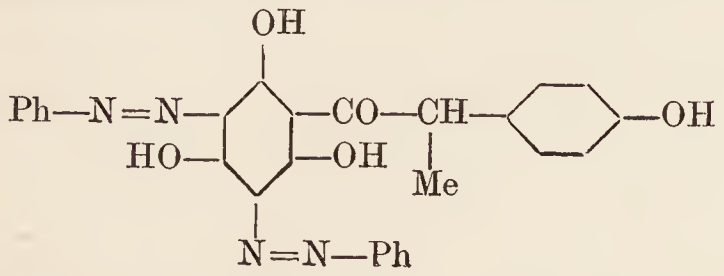
Trimethyl-phloretin $C_{18}H_{20}O_5$ yellow plates, m.p. 152°, obtained by treatment of phloretin with methyl iodide and methyl alcoholic caustic potash, is accompanied, in the reaction product, by

Tetramethyl-phloretin $C_{19}H_{22}O_5$ which can be obtained from the mother liquors after the separation of the trimethyl ether. It forms yellow plates, m.p. 58°, and by treatment with hydriodic acid loses one methoxy group, passing to the trimethyl ether.

A. G. Perkin and Martin (Chem. Soc. Trans. 1897, 1152) have prepared the following dis-azo-derivatives of phloretin:—

[1] Christianite of French authors, their phillipsite being the copper mineral bornite.

Phloretin-disazo-benzene $C_{15}H_{12}O_5(C_6H_5N_2)_2$ produced by adding excess of a solution of diazo-benzene sulphate to a solution of phloretin in aqueous sodium carbonate, and consists of glistening red needles, m.p. 254°–256° (decomp.). To this compound Perkin assigns the structure—



When acetylated by boiling with acetic anhydride and sodium acetate this substance yields *acetyl-phloretin-disazo-benzene*, orange-red needles, m.p. 217°–219°. It is sparingly soluble in acetic acid, and does not dissolve readily in cold dilute alkalis, but warm alkalis dissolve it, forming orange-red solutions which deposit the free azo compound on acidification.

Phloretin-disazo-o-toluene crystallises in red needles, m.p. 250°–251°. A. G. P.

PHLORIDZIN *v.* GLUCOSIDES.

PHLOROGLUCINOL *v.* KETONES and PHENOL AND ITS HOMOLOGUES.

PHLOROL. The name originally given by Hlasiwetz (Annalen, 1857, 102, 166) to the homologue of phenol obtained by the dry distillation of barium phloretate, and shown by Oliveri (Gazz. chim. ital. 1883, 13, 264) to be identical with *o*-ethylphenol. The term is also applied to the mixture of xylenols that occur with creosol in the fraction of creosote of b.p. 217°–220° (Marasse, Annalen, 1869, 152, 75).

PHLOSCEÏNE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PHOCENIC ACID. A name given by Chevreul to *iso*valeric acid.

PHŒNICITE. *Basic lead chromate* (*v.* CHROMIUM).

PHŒNIN and **PHŒNICEIN.** Phœnin, $C_{14}H_{16}O_7$, the glucoside of the leuco compound of phœnicein, is found in the bark parenchyma cells of the *Copaifera bracteata* (Benth.) (purple wood), and crystallises from water in minute colourless needles or rods, which, on standing in air, develop a faintly violet tint. By boiling with methyl alcohol and hydrochloric acid phœnin is converted into phœnicein, and on addition of water to the acid solution is deposited as a red powder soluble in ammonia, with a violet-blue coloration. Purple wood yields approximately 2 p.c. of phœnicein. A. G. P.

PHŒNIX POWDER *v.* EXPLOSIVES.

PHONOLITE or **Clinkstone** (Ger. Phonolith, Klingstein). Fine-grained volcanic rocks composed essentially of sanidine (potash-felspar) and nephelite (or leucite in leucite-phonolite), together with some ferro-magnesian mineral (generally green augite, aegyrite, or hornblende). They are the volcanic equivalents of the nepheline-syenites, being richer in alkalis than trachytes which otherwise they resemble; they contain Na_2O 6–10 p.c., K_2O 4–10 p.c., with SiO_2 55–60 p.c. Their colour is usually light greyish; sp.gr. 2·5–2·6. They are very compact and elastic, and the slabs into which the rock breaks give a ringing sound when struck with a hammer (hence the name, from *φονή*, sound, and *λίθος*, stone). The nephelite, which carries part of the potash, is readily dissolved from the powdered rock by hydrochloric acid. Phonolites are found in northern Bohemia, the Eifel, Auvergne, near Rome, Brazil, &c. In Britain they have been met with at Traprain Law in Haddingtonshire, Eildon Hills in Renfrewshire, and the Wolf Rock off the Cornish coast. The rock is occasionally used locally for buildings and roads, and also as a fertiliser (Krische, Chem. Zeit. 1910, 34, 387). L. J. S.

PHOSGENE GAS. J. Davy's name for carbonyl dichloride or carbon oxychloride, *v.* CARBON.

PHOSGENITE or **Cromfordite.** Chloro-carbonate of lead $PbCl_2 \cdot PbCO_3$, crystallised in the tetragonal system. The crystals are well-developed, often of large size, colourless and transparent, and with a brilliant adamantine lustre. Sp.gr. 6·1–6·2; H. 3; refractive indices (Na) $\omega = 2{\cdot}118$, $\epsilon = 2{\cdot}145$. The mineral is found as brilliant crystals in cavities of corroded galena at the Monteponi lead mine and elsewhere in Sardinia, at Cromford, near Matlock, in Derbyshire, Dundas in Tasmania, and in Upper Silesia. Crystals of recent formation have been observed in lead pipes of the Roman period at the hot saline springs of Bourbonne-les-Bains in France, and in Roman lead slags exposed to the action of sea-water at Laurion in Greece. Phosgenite, and the corresponding bromine compound, $PbBr_2 \cdot PbCO_3$, have been prepared artificially as crystals. It may be synthesised by heating a mixture of lead hydroxide and phosgene at 175° for 1–4 hours. The product is crystalline and of a faint yellow colour. The name phosgenite is from phosgene, because the mineral contains the elements carbon, oxygen, and chlorine. Cromfordite is from the English locality where the mineral was first found. L. J. S.

PHOSOT *v.* SYNTHETIC DRUGS.

PHOSPHATOL. Guaiacol phosphite

$$P(O \cdot C_6H_4 \cdot OCH_3)_3$$

Used in the treatment of tuberculosis.

PHOSPHINE. A syn. for phosphoretted hydrogen PH_3, *v.* PHOSPHORUS. Used also to designate the nitrate of chrysaniline or diamino-phenylacridine $C_{19}H_{15}N_3 \cdot HNO_3$, *v.* CHRYSANILINE.

PHOSPHOMOLYBDIC ACID *v.* MOLYBDENUM.

PHOSPHOR BRONZE *v.* TIN.

PHOSPHORITE and **ROCK-PHOSPHATE.** General terms applied to compact or indistinctly crystallised forms of calcium phosphate, of varying degrees of purity, which are often regarded as massive varieties of the mineral apatite (*q.v.*). It is probable, however, that several allied mineral species are represented, and that the material is usually a mixture of these, together with various impurities. The materials are, in fact, more of the nature of rocks rather than simple minerals.

The term phosphorite, first used by R. Kirwan in 1794 as a synonym of apatite, is more properly restricted to the concretionary and stalactitic masses with a mamillated form externally and often a minutely radio-fibrous or convoluted structure internally. Such material, although often containing calcium fluoride in addition to calcium phosphate, differs

from crystallised apatite in containing a small proportion of calcium carbonate and water. Phosphorite is generally found filling pockets or veins in limestone; for example, in Estremadura and Quercy; and in the Pacific and West Indian islands it has obviously been formed by the action of phosphatic solutions, leached from guano, on the underlying coral-limestone.

A. Lacroix (Compt. rend. 1910, 150, 1213, 1388; Minéralogie de la France, 1910, 4, 555; *cf.* W. T. Schaller, Bull. U.S. Geol. Survey, 1912, No. 509, 89), from a microscopical study of the French phosphorites, separates them from apatite, and places them in a separate division of his classification comprising combinations of phosphates and carbonates. In this division he recognises as species:—

Dahllite, $2Ca_3(PO_4)_2 \cdot CaCO_3 \cdot \frac{1}{2}H_2O$.

Francolite (and its fibrous variety staffelite, or 'hydroapatite'),

$$(CaF)_2Ca_8(PO_4)_6 \cdot CaCO_3 \cdot H_2O.$$

Collophanite $\begin{cases} x[Ca_3(PO_4)_2] \cdot yCaCO_3 \cdot zH_2O. \\ x[(CaF)_2Ca_3(PO_4)_6] \cdot yCaCO_3 \cdot zH_2O. \end{cases}$

The fibres of both dahllite and staffelite are optically uniaxial (or nearly so), with a negative birefringence a little greater than that of apatite. Collophanite is amorphous (colloidal) and optically isotropic; and with its vitreous to resinous lustre and conchoidal fracture resembles opal or gum in appearance. Only exceptionally, however, do any of these minerals occur alone in the French phosphorites; as a rule, they form interbanded mixtures, so intimately that a mechanical separation of them is impossible. For this type of mixed phosphorite the name *quercyite* is proposed; quercyite-α when the crystalline element is optically negative, and quercyite-β when it is optically positive (the crystalline element in the latter case not corresponding with any known species).

W. T. Schaller (J. Washington Acad. Sci. 1911, 1, 151; Bull. U.S. Geol. Survey, 1912, No. 509, 98) gives the following formulæ for the phosphorite minerals:—

Dahllite . .	$9CaO \cdot 3P_2O_5 \cdot CaO \cdot CO_2 \cdot H_2O$.
Francolite . .	$9CaO \cdot 3P_2O_5 \cdot CaF_2 \cdot CO_2 \cdot H_2O$.
Collophanite .	$9CaO \cdot 3P_2O_5 \cdot CaO \cdot CO_2 \cdot H_2O + nH_2O$.
Fluorapatite .	$9CaO \cdot 3P_2O_5 \cdot CaF_2$.
Hydroxyapatite .	$9CaO \cdot 3P_2O_5 \cdot CaO \cdot H_2O$.

The following analyses, by Pisani, are given by Lacroix; in these it is seen that the differences in composition are only slight. I, Dahllite from Mouillac, Tarn-et-Garonne. II, Collophanite from Pouzillac, Gard. III, Quercyite-α from Mouillac, Tarn-et-Garonne. IV, Quercyite-β from Mouillac. V, Quercyite from Castillo de Belmez, prov. Cordova, Spain.

	I.	II.[1]	III.	IV.	V.
P_2O_5 .	38·40	37·40	37·60	36·60	37·75
CaO . .	53·65	49·73	51·85	50 45	52·50
F . .	(2)	0·88	1·50	0·83	(2)
CO_2 . .	5·30	3·75	4·00	4·62	5·70
H_2O . .	2·10	7·05	4·80	6·00	3·20
$Fe_2O_3 \cdot Al_2O_3$	0·57	0·50	—	1·30	0·85
	100·02	99·61	99·75	99·89	100·00
Sp.gr.	2·97	2·69–2·77	2·83–2·87	—	—

In the rock-phosphates occurring as nodules, pebbles, and coprolites in sedimentary rocks, or simply as impregnations of phosphatic material in the rocks themselves, the mineralogical identity of the material is still less definite. For details of occurrence and production, *see* the article FERTILISERS.

Ref.—G. P. Merrill, The Non-metallic Minerals, 2nd ed., New York, 1910. O. Stutzer, Die wichtigsten Lagerstätten der 'Nicht-Erze,' 1911, i. 265–462. X. Stainier, Bibliographie générale des gisements de phosphates, 2nd ed., Annales des Mines de Belgique, vii. 1902 *et seq.* F. Wyatt, The Phosphates of America, 5th ed., New York, 1894. A. Deckers, Étude complète sur les phosphates, Liége, 1894. J. J. H. Teall, The Natural History of Phosphate Deposits, Proc. Geol. Assoc. 1900, 16, 369. Reports on the geological investigations of phosphorite deposits (Russ.) edited by J. V. Samoilov, Moscow, 1909–1915, vols. i.–vii. H. Ries, Economic Geology, New York, 1916. R. J. Jack, The phosphate deposits of South Australia, Geol. Survey S. Austr., 1919, Bull. 7. Phosphates (1913–1919), Imp. Min. Resources Bureau, London, 1921. L. J. S.

PHOSPHORUS. Sym. P. At.wt. 31·02 (Baxter and Moore). From $\phi\hat{\omega}s$, light; and $\phi\acute{\epsilon}\rho\omega$, I bear. Phosphorus was discovered by an alchemist named Hennig Brand, of Hamburg, in 1669, whilst distilling evaporated urine with sand in clay retorts. He is said to have sold the secret of its preparation to Kraaft, from whom it appears that Johann Kunckel learnt what he knew, and published in 1678, in his pamphlet *Oeffentliche Zuschrift vom Phosphor Mirabile und dessen leuchtenden Wunderpilulen.* Kraaft exhibited it as one of the wonders of nature to various crowned heads, among them to King Charles II. of England, in 1677. Kraaft was not a chemist, but seems to have informed Boyle that the phosphorus he exhibited was produced from "somewhat that belonged to the human body," and Boyle eventually succeeded in preparing it, apparently by Brand's method, as he describes in a paper deposited with the Royal Society in 1680, and published after his death. Its manufacture in London was continued by his laborant Godfrey Hankewitz, and it came into commerce as English or Boyle's phosphorus, to distinguish it from the Bolognian, or Baldwin's phosphori-substances which also have the property of luminescence. The early volumes of the Philosophical Transactions contain papers by Slare and others in which many of the properties of phosphorus are accurately described.

It was an expensive substance owing to the difficulty of its preparation by Brand's process, and was not commonly known until nearly a century later, when Gahn, in 1769, showed that calcium phosphate was the main constituent of bone ash, and Scheele devised a process for preparing it from that material.

Scheele's method of producing phosphorus, first published in 'Gazette Salutaire de Bouillon' in the year 1775, consisted in dissolving bone ash in nitric acid, and then removing the lime as sulphate with sulphuric acid; but this method was afterwards simplified by Nicholas and Pelletier, who decomposed the bone ash direct by sulphuric acid, and was further improved by Fourcroy and Vauquelin, who determined the exact quantity of sulphuric acid required for the complete decomposition of bone ash.

[1] Also Na_2O, K_2O, 0·30.

[2] A little fluorine included with the Fe_2O_3,Al_2O_3.

From the fact of the presence of phosphorus in bones, its universal diffusion in nature might have been suspected. In fact, upon a soil free from phosphorus no plant can grow, as its presence is essential to the formation of the plant structure, and is found in largest quantities in the seed and fruit. Phosphorus, likewise, is necessary for the growth and nutrition of the animal tissues, and is present both in the substance of the brain and in the nervous matter connected therewith. It ranks, therefore, with oxygen, nitrogen, hydrogen, carbon, &c., as one of the elements necessary to the building up of the animal and vegetable body. Besides being present in all fruitful soils, phosphorus is found in most springs, in all rivers, and in the sea. At one time phosphorus was considered to be a compound body containing ' phlogiston ' and an acid, till Lavoisier showed that when it is burnt in air the acid produced weighs more than the phosphorus itself, the increase in weight being due to the oxygen of the atmosphere with which the phosphorus had combined (Opuscules Physiques et Chimiques, 1774).

Manufacture of Phosphorus.—Some form of calcium phosphate, such as bone ash, precipitated phosphate obtained as a by-product in the manufacture of glue from bones, or naturally occurring phosphates, such as the various forms of apatite, Sombrero, Redonda and Charleston phosphates, &c., constitutes the raw material from which phosphorus is still obtained. But Scheele's method, or the modifications of it which were subsequently devised, are no longer employed. These consisted, in principle, in decomposing calcium phosphate with an acid, usually sulphuric acid, separating the precipitated calcium sulphate, concentrating the phosphoric acid liquor, mixing it with charcoal, coke, or sawdust, and strongly heating the dried mixture in clay retorts, whereby the orthophosphoric acid, H_3PO_4, is converted into metaphosphoric acid, HPO_3, which, at a high temperature, in contact with carbon, is resolved into phosphorus, carbon monoxide, and hydrogen :

$$4HPO_3+12C=P_4+2H_2+12CO$$

Full details of this practically obsolete method were given in the last edition of this work.

The success of the application of electricity to the production of certain metals and alloys, notably those of aluminium, led Readman to try that source of energy for the production of phosphorus, and the result was that, along with T. Parker (who applied for letters patent only a few weeks after Readman's application) (Readman's patent, 14962, Oct. 18th, 1888 ; Parker and Robinson's patent 17719, Dec. 5th, 1888), a process was devised, called the Readman-Parker and Robinson system, which effects the *continuous* production of phosphorus *direct* from raw materials by means of the electric furnace, the heat being applied in and through the phosphorus-bearing mixture in the furnace, and not, as in the case of distillation, in retorts, heated from the outside, involving, in consequence, a great expenditure of fuel.

The process is carried out as follows. The phosphate, carbon, and silica, in proper proportions and all carefully and intimately mixed together, are introduced (previously heated to as high a temperature as possible) into the upper part of the electric furnace by means of a tight-fitting hopper arrangement, and the electric current is led to and from the furnace by copper cables connected to large carbon electrodes situated on either side of the furnace. The furnace itself is practically an iron tank, lined inside with refractory bricks, thus making a kind of brick-sided trough about 18 inches square and 36 inches deep, closed at the top by the hopper referred to, and having an outlet pipe to the condenser placed on the upper part of the side of the furnace.

After charging the furnace, the current is turned on, and indications of phosphorus may soon be seen in the condensers. The gases escaping by the side pipe pass on to a series of copper condensers, the first of which contains hot and the others cold water, when they are allowed to escape into the air. As the phosphorus is distilled off from the mixture the residue in the furnace forms a liquid slag, which from time to time is tapped out at the bottom of the furnace, fresh phosphorus-bearing mixture being introduced by the hopper at the top precisely as in blast-furnace practice, where closed tops are used. In this way the operation is made continuous, and is carried on for days without cessation.

The distillation begins at 1150° and requires a temperature of 1400° to 1500° to complete the process.

$$2Ca_3(PO_4)_2+6SiO_2+10C=6CaSiO_3+10CO+P_4$$

In the Irvine modification of this process either calcium or aluminium phosphate can be used with the silica or basic salt flux. The Oldbury Electro-Chemical Company now employs a total of 8600 h.p. for the manufacture of phosphorus at Niagara Falls. The Landis Furnace (U.S. Pat. 842,099 (1907); Electrochem and Metall. Ind. 1907, 5, 55), which differs in details from those just described, employs the same principle, and is said to be operated by the American Phosphorus Company at Yorkhaven, Pa. (Pring's Electric Furnace, Longmans, Green and Co., 1921).

The Crude Phosphorus.—The phosphorus obtained in the condensers varies in colour from a pale buff to a brick-red, chocolate, or nearly black, colour. The colour is due to impurities, as well as to the presence of lower oxides of phosphorus and amorphous phosphorus. If condensed in *cold* water, it resembles the raspings of cork and floats on water. In this condition it is much more inflammable than it is in a pure state, and great care must be observed in handling it.

The crude phosphorus is first melted under water in a small lead-lined agitating pan provided with a lead steam-coil, and from 3–4 p.c. of potassium or sodium dichromate, previously dissolved in water, is added. Sulphuric acid in equivalent proportion is next run into the agitator, and the whole is left for 2 hours or more. After that time the phosphorus should be of a pale-yellow colour and almost transparent. The chrome liquors are carefully removed, and the phosphorus then receives a washing with hot water, after which it is syphoned off and rapidly filtered through a canvas filter-bag to remove mechanical impurities. It is now ready for moulding.

(*k*) *The Moulding.*—The phosphorus melted under hot water may be cast into 'wedges,' or made into 'sticks.' The 'wedges' or 'pains' (of the French manufacturer) are easily made. The liquid phosphorus is ladled under hot water into tin moulds $10\frac{1}{2}$ ins. diameter by $4\frac{1}{2}$ ins. deep, standing in a row in a shallow trough, and while still liquid a star-shaped arrangement, made also of tin, is dropped into the mould. The object of this is to divide the circle equally into 10 sectors or wedges. On solidifying the phosphorus by running in cold water into the trough and then removing it from the mould, 10 separate wedges are obtained in a convenient form for packing, each wedge weighing about 2 lbs. To admit of easy removal of the phosphorus, the tin mould divides into 2 parts and is made tight by india-rubber joints and flanges, &c.

If the phosphorus is desired in the form of 'sticks,' the fused element is drawn through

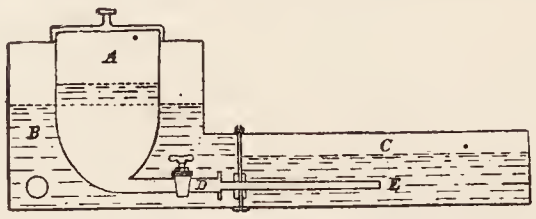


FIG. 1.—SECTION OF APPARATUS FOR MOULDING PHOSPHORUS INTO STICKS.

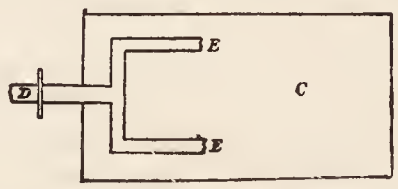


FIG. 2.—PLAN OF COLD WATER TANK FOR MOULDING PHOSPHORUS INTO STICKS.

A. Pot for melting phosphorus under water. H. Hot water tank heated with steam coil. C. Cold water tank, flanged to B. D. Cock for escape of liquid phosphorus. E. Metal tubes. (Same letters apply to Figs. 1 and 2.)

glass tubes in an apparatus illustrated by the sketches (Figs. 1 and 2).

Another method of moulding is to run the liquid phosphorus into slightly-tapered tin tubes made of a length to suit the tin packing-cases. The tubes are closed at one end by corks, and are set (corked end down) in troughs containing hot water, when the tubes are filled with the molten phosphorus. Cold water is run into the trough to solidify the latter, which is then removed from the moulds.

(*l*) *The packing.*—The 'wedges' are packed along with water in tin cylinders, holding 50 kilos. of phosphorus. The dimensions of the cylinders are 22 ins. deep by 11 ins. diameter. The lids (11 ins. diameter) are loose, but fit tightly inside, and have a $\frac{3}{4}$-inch hole, through which water is poured after the lids are soldered on. These small holes are finally soldered up, and the cylinder is thus hermetically sealed and completely filled with water. Another size of case sometimes employed holds 25 kilos.; it is 12 ins. deep by 11 ins. diameter.

The tin packing cylinders should be provided with three wire handles—two opposite one another—at the upper part, and the third lower down near the base. These are found convenient in handling.

The sealed tins are now packed along with sawdust in rectangular wooden boxes 24 ins. long by $12\frac{1}{4}$ ins. broad $\times$ $12\frac{1}{4}$ ins. deep. The wood is pine $\frac{5}{8}$ in. thick. The boxes should be strengthened with hoop-iron at the edges. The sawdust is tightly rammed down between the tin case and the side of the box, and thus makes a firm and safe package.

When exporting phosphorus to certain countries—*e.g.* Germany—the wooden boxes require to be further packed in canvas, and iron handles must be tightly fixed to either end of the box for convenience in lifting.

The 'stick' phosphorus is packed along with water in tins which hold 10 lbs. each. The tins are $7\frac{5}{8}$ ins. long by $5\frac{5}{8}$ ins. diameter; each one holds about 90 sticks ($7\frac{1}{2}$ ins. long by $\frac{1}{2}$ in. diameter).

The lids, &c., are soldered on as before described. These tins are further packed as in the case of 'wedges,' in wooden boxes holding ten in a box.

Properties of Ordinary Phosphorus.—Phosphorus at the ordinary temperature when pure is a colourless, soft and flexible, translucent, waxy-looking solid, which becomes hard and brittle at temperature below 5·5°. It is extremely inflammable, especially if not quite pure, and must always be kept under water. It has a great affinity for the oxygen of the air with which it combines directly.

It does not combine with liquid oxygen, but after removal from the liquid, explodes with great violence when struck, or touched with hot iron, or subjected to the action of an electric spark (Piutti).

It also combines *directly* with chlorine, bromine, iodine, and sulphur, but not with nitrogen and hydrogen.

Phosphorus is luminous in the dark, and in a moist atmosphere a gradual oxidation takes place with formation, first of phosphorous acid, and ultimately of phosphoric acid, ozone and hydrogen peroxide being likewise produced at the same time. According to Weiser and Garrison (J. Phys. Chem. 1921, 25, 349, 473) gaseous ions are formed during the oxidation of phosphorus, and these account for the conductivity of 'phosphorised air.' These ions furnish nuclei about which oxides and water vapour condense forming clouds. The cloud arising from glowing phosphorus contains equal numbers of positive and negative particles if the phosphorus is not charged. Ions are formed in the reaction zone and may be withdrawn by an electric field against a current of air sufficiently rapid to remove oxide particles and ozone. The luminescence of phosphorus is not changed appreciably by charging the element. The darkening of a photographic plate protected from light in the region of glowing phosphorus is due to the action of hydrogen peroxide and the vapour of phosphorous oxide, and not to anything in the nature of radium rays or of phosphorus 'emanation.' The complete oxidation of phosphorus takes place in two stages, phosphorous oxide being the intermediate product. The first step in the oxidation takes place without the emission of light; the luminescence of oxidising phosphorus is due to the oxidation of phosphorous oxide. Ozone is formed during the oxidation of phosphorous oxide, and it is produced also by the ultra-violet light emitted by glowing phosphorus. The vapours of a number of organic compounds influence the rate of oxidation of phosphorus. Most of the vapours

retard the oxidation, but nitrobenzene and diphenylamine accelerate it as the adsorbed vapours react with these substances. The rapid oxidation of phosphorus to phosphorous oxide occurs at 27° in pure oxygen under 1 atmos. pressure, whilst that of phosphorous oxide to phosphoric oxide under the same conditions occurs at 65°. As a rule, the heat of the reaction of the first step raises the temperature in the reaction zone to the point where the phosphorous oxide oxidises with sufficient velocity to emit light (Chem. Soc. Abst. 1921, ii. 637, 695). The spectrum of the phosphorus glow shows 14 sharp lines in the ultra-violet, and a band in the neighbourhood of 3252 Angström units (Centnerszwer and Petrikaln, Zeitsch. physikal. Chem. 1912, 80, 235). When exposed to daylight, under water, a whitish incrustation is formed, which frequently becomes of a reddish hue. According to Baudrimont (Compt. rend. 61, 857, 1866), the crust is formed only under influence of oxygen, and possesses all the usual properties of ordinary phosphorus. Sp.gr. at 16°, 1·82.

Phosphorus melts at 44·5° to a colourless liquid. The exact melting-point depends to a large extent on the rate of heating. If left undisturbed in a smooth glass vessel it may remain liquid at temperatures considerably below the melting-point. It boils at 290° under atmospheric pressure, the vapour being colourless, and takes fire in air when heated to 34°. Its crit. temp. is 948° (abs.) crit. pressure 80 atmos. (van Laar). Its vapour pressure between 44° and 150° may be expressed by $P=7{\cdot}9542-2757{\cdot}5/T$, P being the pressure in mm. of mercury (McRae and van Voorhis, J. Amer. Chem. Soc. 1921, 43, 547). Phosphorus vapour when superheated and then cooled rapidly condenses, partly as red phosphorus. The process appears to comprise first dissociation $P_4 \gtrless P_2$ and then union of P_4 and P_2 mols. to form mols. of red phosphorus:

$$xP_2+yP_4=P_{2x+4y}.$$

Ordinary phosphorus is very soluble in carbon disulphide, one part dissolving 9·26 parts of phosphorus, a slight amount of heat being developed, but on cooling to ordinary temperatures some of the phosphorus is precipitated in a crystalline form. Phosphorus is also very soluble in sulphur chloride, phosphorus trichloride, and phosphorus sulphide. It is nearly insoluble in water.

The following table shows the weight of different solvents required to dissolve 1 part by weight of phosphorus. The temperature of the solvent, unless otherwise stated, is 12°:—

	Parts
Benzene (90 p.c. sp.gr. 0·878)	82·5
Chloroform	83
Aniline	154
Oil of turpentine	162
Paraffin oil (sp.gr. 0·806)	179
Ethyl ether (sp.gr. 0·725)	203
Olive oil	649
Alcohol (sp.gr. 0·801)	764
,, ,, ,, at 40°	535
Wood spirit (sp.gr. 0·846)	1408
,, ,, ,, ,, at 40°	862
Acetone	2702
Solution of caustic soda (sp.gr. 1·35)	194
Liquor ammoniæ (sp.gr. 0·880)	3030

The ammoniacal solution becomes dark brown, and the surface of the phosphorus is coated with a brown-black deposit. When water is added to the greater number of the above solutions, the phosphorus is precipitated.

Cold concentrated nitric acid dissolves phosphorus. If exposed to the action of dilute nitric acid for some time its crystalline character becomes evident.

Sulphuric acid (92 p.c. O.V.) does not dissolve phosphorus in the cold, but attacks it on prolonged boiling. Phosphorus is insoluble in cold concentrated hydrochloric acid.

Phosphorus fumes in the air, emitting a garlic-like odour. On exposure to air, it not unfrequently melts and takes fire, and during combustion dense white fumes of phosphoric oxide are produced, which can be collected in snowy flakes. The burns produced by ignited phosphorus are of a serious nature, and are very slow in healing, any unconsumed phosphorus left on the wound being most difficult and painful to remove.

Phosphorus sometimes contains a small proportion of arsenic derived from the sulphuric acid used in the preparation of the phosphoric acid. If this be present in any quantity the refined phosphorus has a red or mahogany colour. Phosphorus is a powerful poison; less than 2 grains are said to have caused death. Those who have to handle it frequently are liable to necrosis, which begins with the disintegration of the jaw-bones, and ends with their total destruction. Ill-fed and scrofulous persons are said to be specially affected.

Phosphorus does not conduct electricity (Faraday).

According to Deville and Troost, the vapour of phosphorus has a sp.gr. of 4·50 at 1040°.

At temperatures between 500° and 700° the vapour density corresponds with P_4. At higher temperatures dissociation takes place, but even at 1200° it is only 61 p.c. under a pressure of 175 mm. Calculations on the assumption that dissociation occurs in accordance with the equation $P_4 \gtrless 2P_2$ agree with experiment. Under atmospheric pressure the degrees of dissociation at 800°, 1000°, and 1200° are respectively 0·01, 0·1, and 0·33; under a pressure of 0·25 atmos. the degree of dissociation is almost 0·66 at 1200° (Stock, Gibson and Stamm, Ber. 1912, 45, 3527). According to Preuner and Brockmöller (Zeitsch. physikal. Chem. 1912, 81, 129) the vapour changes from P_4 through P_2 to P_1 on being heated from 600° to 1200°. The change from gaseous P_4 mols. to $2P_2$ mols. absorbs 31,500 cal. and from P_2 mols. to $2P_1$ mols. by an absorption of 45,500 cal. Rapid cooling of phosphorus vapour deposits a mixture of the yellow and scarlet modification; slow cooling deposits the pure yellow modification.

Phosphorus is tough, and cannot be pulverised; but if melted under water and shaken until the fluid is quite cold, it forms round pellets of various sizes; an aqueous solution of urea or alcohol aids this formation. When heated with aqueous vapour to a temperature of 250°, phosphorus decomposes the water, phosphorous acid and phosphoretted hydrogen being formed.

Phosphorus volatilises to a small extent when boiled with water. *In vacuô* it volatilises at ordinary temperatures. It is not luminous in

pure oxygen at temperatures below 20° (Müller); but if mixed with a neutral gas, or if it be rarefied, then luminosity at once results (Graham). It volatilises in pure oxygen without oxidation as it does in other gases, and obeys Dalton's law of partial pressures. In oxygen at 20°, p=0·0251 mm. mercury; in hydrogen at 20°, p=0·0253 mm.; at 25°, p=0·0426; 30°, p=0·0724 mm.; 35°, p=0·0889 mm.; 40°, p=0·1221 mm. (Centnerszwer, Zeitsch. physikal. Chem. 1913, 85, 99). The presence of mercuric chloride and of phenol (Polstroff and Mensching, Chem. News, 57, 71), and of certain gases, such as olefiant gas, hydrogen sulphide, or the vapours of turpentine or ether when present even in small quantities, prevent the glow of phosphorus. Nitrobenzene and diphenylamine work positively in catalysing the oxidation of phosphorus. If a drop of these substances is brought in contact with phosphorus in air, the glow is strengthened, and the phosphorus bursts into flame (*cf.* Rayleigh, Roy. Soc. Proc. 1921, 372). If hydrogen, nitrogen or carbon dioxide in which phosphorus has been exposed be brought into contact with oxygen it becomes luminous from the phosphorus diffused in the gas.

Phosphorus at high temperatures combines with most of the metals, forming phosphides. For example, if calcium phosphate and silica with carbon and iron (as ore or metal) be heated to a high temperature, a very fusible iron phosphide, Fe_2P, can be obtained.

Phosphorus, owing to its affinity for oxygen, is a powerful reducing agent. It precipitates copper, silver, platinum, palladium, and gold when brought into a solution of the salts of these metals.

For the atomic refraction of phosphorus, *see* Kovalevski (J. Russ. Phys. Chem. Soc. 1897, 29, 217); Arbuzov and Ivanov (*idem*, 1915, 47, 2015).

Amorphous phosphorus.—Up to 1845 the 'yellow' or ordinary phosphorus was the only variety known. In that year 'red' or 'amorphous' phosphorus was discovered by Schrötter, although its existence had been previously observed by other chemists who had misunderstood its nature.

Amorphous phosphorus in compact pieces is a reddish-brown, moderately hard substance,[1] somewhat resembling in appearance hematite iron ore. It is opaque, with a slight metallic lustre. It is brittle and easily broken, and exhibits a conchoidal iron-black fracture with sharp edges. When heated it becomes almost black at 500° and melts at *circa* 600° to a yellow mobile liquid. On cooling the colour deepens to reddish-brown until solidification occurs.

The sp.gr. of amorphous phosphorus is 2·25. It is without taste or smell, is unattacked by most solvents, and if taken internally is excreted unchanged.

A pure red variety of phosphorus of a cinnabar colour may be obtained by heating phosphorus tribromide with mercury. It is a micro-crystalline powder D_4^{24} 1·876, which becomes brownish-black at 250° and regains its original colour on cooling. It melts at 592·5±0·5. It is insoluble in carbon disulphide and is not blackened by ammonia, oxidises slowly in moist air and inflames in air at about 300° (Wolf, Ber. 1915, 48, 1272).

As met with in commerce, amorphous phosphorus frequently contains small quantities of ordinary phosphorus, up to about ½ p.c.; in addition, it usually contains phosphoric acid, graphite, and other impurities, and has generally an acid reaction.

Ground amorphous phosphorus dissolves very easily in nitric acid on account of its state of sub-division.

Chlorine has no action on this variety of phosphorus unless the latter is heated, when it burns with a yellow flame.

For ignition, amorphous phosphorus requires a temperature of 430°–440°: probably conversion into ordinary phosphorus precedes ignition.

The conversion of yellow into amorphous phosphorus is effected by heating the former to a temperature between 240° and 250° for some time. The apparatus employed is a cast-iron pot which is closed with a cover. A narrow tube open at both ends is screwed into the upper part of the pot. This acts as a safety valve, and avoids all risk of explosion. If pressure be employed within the pot and the temperature exceeds 300°, the yellow is transformed into amorphous phosphorus in a very short time. There is, however, considerable danger in this treatment which might far outweigh the economy in time. According to the method used, when the conversion is effected in open iron vessels in which the air finds but limited access, the process, though tedious, is free from all difficulty or danger.

The amorphous phosphorus forms hard compact lumps. These are ground under water, and freed from ordinary phosphorus by boiling the powder with a solution of caustic soda; it is then repeatedly washed with boiling water and carefully dried by steam heat. The ground red phosphorus, dried in the manner described, is sent out in the dry state in tin boxes holding 10 lbs. each.

Ordinary phosphorus may also be converted into amorphous phosphorus by chemical action, as by heating it to 200° with a small quantity of iodine, selenium or phosphorus tribromide, or by radiation (sunlight, diffused day-light, quartz-mercury-vapour lamp, induction spark). The action of the red rays and ultra-violet rays is slight; the maximum effect is in the visible violet. Under the action of radiation ordinary phosphorus turns yellow, then red, and loses its transparency. Amorphous phosphorus is produced by heating phosphorus vapour at 900°–1175°, and suddenly cooling it. If the cooling is gradual no red phosphorus is formed. It is soluble in alcoholic solution of potash from which, according to Burgess and Chapman, it is precipitated unchanged on adding an acid. According to Michaelis the red precipitate is the suboxide P_4O.

Red phosphorus when boiled in acid solutions of various salts exerts a strong reducing action. Gold and silver salts are converted into insoluble phosphides; mercurous or mercuric salts are reduced to the metal; palladium and osmium salts are reduced either to the metal or to the phosphide; stannic, ferric and iridic salts are reduced respectively to stannous, ferrous and

[1] The hardness of amorphous phosphorus lies between calcareous spar and fluor spar.

iridous salts. Selenates are reduced either to the element or an insoluble phosphide, molybdates to quadrivalent molybdenum salts, vanadates to trivalent vanadium salts, bichromates to chromic salts and permanganates to manganous salts. Bismuth, lead, cadmium, antimony and arsenic salts, arsenates and stannous salts are not reduced, whilst tellurates and chloroplatinates are only slowly reduced (Rosenstein, J. Amer. Chem. Soc. 1920, 42, 883).

In addition to the red or amorphous variety, there is a third allotropic modification of phosphorus—viz. violet or rhombohedral phosphorus—formed by heating the element in sealed tubes with metallic lead for some hours. On cooling, crystals are found permeating the lead; these are separated by dilute nitric acid, which dissolves out the lead. This phosphorus is a dark crystalline substance, sp.gr. 2·34 at 15·5°.

H. M. Vernon (Phil. Mag., October, 1891) states that a rhombic modification of phosphorus exists, melting at about 45·3°, and of sp.gr. 1·8272. It appears to be formed from the octahedral variety by slowly cooling it when liquid.

Bridgman (J. Amer. Chem. Soc. 1914, 36, 1344; *idem*, 1916, 38, 609), by exposing white phosphorus to high pressure (12,000 kilos) at 200°, has obtained a *black* modification, soluble in carbon disulphide and crystallising in microscopic crystals belonging to the hexagonal system. Sp.gr. 2·691: it is not spontaneously inflammable and may be heated to 400° without igniting. It changes into the scarlet form on being heated at 575°. In its general chemical behaviour it is very similar to red phosphorus, but is much less volatile and is a fairly good conductor of heat and electricity. For a discussion of the system Phosphorus from the point of view of the theory of Allotropy, *see* Smits and Bokhorst (Zeitsch. physikal. Chem. 1916, 91, 249).

Uses of phosphorus.—The chief consumption of phosphorus is in the manufacture of matches, in which it is used as phosphorus sesquisulphide or as red phosphorus. The so-called 'safety' matches which ignite on the box, have no phosphorus on the match itself, but have a thin layer of red or amorphous phosphorus on the sides of the box. *V.* Art. Matches.

Phosphorus is used in medicine in small doses. It is likewise employed in the form of a paste for the destruction of rats and mice. It is also used in the laboratory, and in the manufacture of many organic compounds.

Phosphorus as calcium phosphide is one of the constituents of the material used for distress signalling at sea.

Phosphor bronze, which is now extensively employed in the arts, contains a small percentage of phosphorus, which modifies the properties of copper to a large extent, favourably when present in minute quantities, and unfavourably if present in more than 2–3 p.c.

At the present time, most of the phosphorus manufactured in Europe is made by Messrs. Albright and Wilson, Ltd., of Oldbury, Birmingham, England, Messrs. Coignet and Cie., Lyons, France, and the Chemische Fabrik Griesheim-Elektron, Frankfort-a-Main, Germany. There are makers in Russia, and at Trollhättan and Gullspäng in Sweden, which make sufficient phosphorus by the electrical smelting method to satisfy the needs of the Swedish match industry. Canada and the United States of America, and Japan, are supplied by factories in each of those countries.

Non-metallic Compounds of Phosphorus.

Hydrogen phosphides. Four of these compounds, PH_3, P_2H_4, P_4H_2(?), and P_9H_2, are known, the first being gaseous, the second liquid at ordinary temperatures, and the last solid.

Phosphorus trihydride, phosphoretted hydrogen, or *phosphine*, PH_3, is usually obtained by heating phosphorus with milk of lime or strong potash: $3KHO+3H_2O+P_4=PH_3+3KH_2PO_2$; or by decomposing calcium phosphide with water: $3Ca_2P_2+12H_2O=4PH_3+P_2+6Ca(HO)_2$.

It is also formed by the action of dilute acids on the phosphides of zinc, iron, tin, magnesium and aluminium (Lüpke, Chem. Soc. Abstr. 1891, 397; Matignon, Compt. rend. 1900, 130, 1391). Hydrogen phosphide is also evolved when ordinary phosphorus is acted on by warm water, by hydrogen peroxide, or by sodium hydroxide (Weyl, Ber. 1906, 39, 1307).

As prepared by the action of water on calcium phosphide, the gas contains a sufficient amount of the dihydride, P_2H_4, probably produced by a secondary reaction,

$$Ca_2P_2+4H_2O=2Ca(OH)_2+P_2H_4$$

to render it spontaneously inflammable. When passed through water, each bubble on entering the air gives rise to a vortex ring of phosphoric oxide or metaphosphoric acid. The gas also contains hydrogen produced by the gradual decomposition of the hypophosphite by the alkali: $KH_2PO_2+2KOH=2H_2+K_3PO_4$.

The spontaneous inflammability may be destroyed by decomposing or condensing the dihydride, by exposure to light, or by passage through a tube cooled by a freezing mixture.

The trihydride may be obtained free from the dihydride by decomposing calcium phosphide with hydrochloric acid, which converts any dihydride formed into the gaseous and solid hydrides. It may be prepared pure by decomposing phosphonium iodide with water, or preferably with potash,

$$PH_4I+KOH=PH_3+KI+H_2O$$

(Hofmann, Ber. 1871, 4, 200).

Phosphine may readily be obtained from a specially prepared mixture of calcium and aluminium phosphides by the action of water, the process being completed by the addition of hydrochloric acid. The only impurity in this case is a very small quantity of hydrogen (Matignon and Trannoy, Compt. rend. 1909, 148, 167).

Phosphine is a colourless gas with an offensive, garlic-like smell. Its density is 1·1829; it liquefies at −85°, solidifies at −133·5° (Olzewski) and has the critical temperature 51·3° and the critical pressure 64 atmospheres.

Phosphine may be mixed with oxygen without alteration, but if the pressure of the mixture be suddenly diminished, an explosion occurs. (Compare also Lemoult, Compt. rend. 1907, 145, 374.) The gas also takes fire when brought into contact with dilute nitric acid or if mixed with the vapours of chlorine or bromine water and is decomposed into hydrogen and phosphorus by a series of electric sparks. It is also decomposed by heat at a temperature depending upon the nature of the walls of the

containing vessel. Phosphine is a very poisonous gas, a small quantity, when breathed, producing in turn dyspnœa and death.

It is somewhat soluble in water and is absorbed by solutions of copper sulphate and mercuric chloride and bromide, forming the phosphides of the metals, and in some cases more complex salts (Joannis, Compt. rend. 1898, 127, 270; 1899, 128, 1322, 1398; 129, 336; Rubénovitch, *ibid.* 1898, 127, 270; 1899, 128, 1398; Ribeau, *ibid.* 128, 1452; Lemoult, *ibid.* 1907, 145, 1175; Brukl, Z. Anorg. Chem. 1922, 125, 252).

Like ammonia, it combines with metallic chlorides such as those of tin, antimony, aluminium, &c., and with hydrobromic and hydriodic acids to form *phosphonium* compounds, of which phosphonium iodide, PH_4I, is used as a powerful reducing agent and in the preparation of many organic phosphorus compounds.

Passed into a warm aqueous solution of formaldehyde acidified with hydrochloric acid it yields *tetramethylolphosphonium chloride* $PCl(CH_3{\cdot}OH)_4$, m.p. 151° (Hoffman, J. Amer. Chem. Soc. 1921, 43, 1684).

Gattermann and Haussknecht (Ber. 1890, 1174) employ the following process for preparing *phosphorus dihydride.* A large three-necked Woulff's bottle, three-fourths filled with water, is freed from air by a current of hydrogen supplied through a tube fitted in one neck and dipping just beneath the water, and is heated in a waterbath to 60°. Calcium phosphide is then introduced in lumps weighing about 2 grams through a wide, funnel-topped tube fitted to the second neck and just dipping beneath the water. The evolved gases pass through a tube fitted to the third neck to a test-tube, from which passes a tube to a condensing-tube surrounded by iced water. The water in the gas condenses in the test-tube, and the hydride, P_2H_4, liquefies in the condenser, about 2 c.c. being obtained from 50 grams of calcium phosphide. The uncondensed gas may be passed through a flask containing hydrochloric acid, which decomposes the remaining P_2H_4 into the trihydride and the solid hydride.

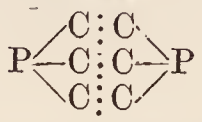
The dihydride is a colourless liquid of sp.gr. 1·007 at 12°, boiling, when not too suddenly heated, at 57°–58° (735 mm.) (Gattermann and Haussknecht, *l.c.*). On exposure to light, or under the action of hydrochloric acid, it decomposes into the trihydride and the solid hydride. Small quantities of the dihydride impart spontaneous inflammability to hydrogen, carbon monoxide and other combustible gases.

The *solid hydride* is obtained, as above, as a yellow powder, by decomposing the dihydride with hydrochloric acid, or by the action of light, or by treating calcium phosphide with hot hydrochloric acid, or by treating calcium phosphide with water and allowing the gas formed to come in contact with calcium chloride (Stock, Böttcher and Lenger, Ber. 1909, 42, 2839). It ignites when heated in the air.

After exposure to the air, it acquires an acid reaction and the odour of phosphine. It is quite stable in the dark, but in sunlight it becomes red and evolves an inflammable gas. In a vacuum it evolves pure phosphine, and this is recommended as a method of preparing the latter by Stock, Böttcher and Lenger (*l.c.*). The red substance which remains behind is, according to these authors, P_9H_2, produced thus, $5P_{12}H_6=6P_9H_2+6PH_3$. The hydride P_9H_2 is stable in dry air, but in moist air it decomposes forming phosphine and phosphoric acid. It dissolves in liquid ammonia forming a black compound varying in composition between P_9H_2,NH_3 and $2P_9H_2,NH_3$ (*ibid.* 2847).

Similar black compounds are produced by the union of the solid hydride $P_{12}H_6$ with ammonia and piperidine (Schenck, Ber. 1903, 36, 4202; Stock, *ibid.* 1903, 36, 1120; Stock, Böttcher and Lenger, *l.c.*).

A **carbide of phosphorus,** P_2C_6, or



is formed by the action of phosphorus trichloride on the compound I.Mg.C:C.Mg.I in ethereal solution. It is a white amorphous compound which inflames when warmed in air, giving phosphorus pentoxide and carbon dioxide (De Mahler, Bull. Soc. chim. 1921, [iv.] 29, 1071).

Compounds of Phosphorus and Nitrogen.

A considerable number of these compounds are known.

Phosphorus nitride P_3N_5 can be obtained quantitatively and absolutely pure by saturating pure phosphorus pentasulphide with pure dry ammonia at the ordinary temperature, subsequently heating the products in an atmosphere of hydrogen, then in a current of ammonia at 850° (Stock and Hoffmann, Ber. 1903, 36, 314; Stock and Grüneberg, *ibid.* 1907, 40, 2573; Stock and Johannsen, *ibid.* 1908, 41, 1593). It varies in colour from pure white to dark red, according to the time of heating in its preparation and has sp.gr. of 2·51 at 18°. At the ordinary temperature it is inactive, but acts as a powerful reducing agent at a high temperature. It is decomposed by many metals and by water at 180°. When heated in chlorine or oxygen it takes fire.

Phospham PN_2H or N:P:NH is obtained as an amorphous, light, white powder, insoluble in water and infusible at a red heat, when the product of the reaction of ammonia on phosphorus pentachloride is heated in the absence of air until fumes of ammonium chloride cease to be evolved (Besson, Compt. rend. 1892, 114, 1264; Besson and Rosset, *ibid.* 1908, 146, 1149). When dry, it is oxidised by heating with silver oxide, evolving half of its nitrogen in the form of nitrogen compounds, the other half in the elementary condition; if previously moistened it decomposes thus:

$$3PHN_2+9H_2O=3HPO_3+6NH_3$$

Phosphoramide $P(NH_2)_3$ is obtained by the action of ammonia on phosphorus tribromide or triiodide at −70° (Hugot, Compt. rend. 141, 1235). It is an unstable yellow solid which readily decomposes at 0°, forming *phosphorimide*, $P_2(NH)_3$, a brown solid which decomposes on heating into ammonia, nitrogen, and phosphorus (*v.* also Stock, Ber. 1903, 36, 1120).

Phosphamide (*phosphodiamide*) $PO(NH)NH_2$ is a white powder obtained by the action of water

on the product of the action of ammonia on phosphorus pentachloride :

$$PCl_3+4NH_3=(NH_2)_2PCl_3+2NH_4Cl$$

and

$$(NH_2)_2PCl_3+H_2O=PO(NH)NH_2+3HCl$$

Phosphoryl triamide (*phosphotriamide*) $PO(NH_2)_3$ is a white amorphous powder obtained by the action of dry ammonia on phosphorus oxychloride (Schiff, Zeitsch. öffentl. Chem. 5, 609).

Phosphorus diamide $POH(NH_2)_2$ is obtained by the action of ammonia on a solution of phosphorous oxide in ether or benzene. It is a white powder which dissolves in water with incandescence and is violently decomposed by dilute hydrochloric acid, forming phosphine, phosphoric and phosphorous acids, ammonium chloride and phosphorus (Thorpe and Tutton, Chem. Soc. Trans. 1891, 1027).

Phosphamidic acid or **amidophosphoric acid** $PO{\cdot}NH_2(OH)_2$, is formed by the action of dry ammonia on phosphorus pentoxide (Biltz, Ber. 1894, 27, 1257) ; or the potassium salt of the acid is obtained by the action of potassium hydroxide on the corresponding phenyl ester, the free acid being formed by the decomposition of the lead or silver salt by hydrogen sulphide and precipitating it from the filtrate with alcohol (Stokes, Amer. Chem. J. 1893, 15, 198 ; 16, 154). It forms colourless microscopic crystals having a sweet taste and forming both normal and acid salts.

Diamidophosphoric acid $PO(NH_2)_2OH$, is a crystalline compound obtained in the same way as the foregoing acid (Stokes, Ber. 1894, 27, 565). It forms the silver salts $(NH_2)_2PO{\cdot}OAg$ and $(NHAg)_2P(OAg)_3$.

A number of imido phosphoric acids have also been prepared (Stokes, Amer. Chem. J. 1896, 18, 629 ; 1898, 20, 740).

Phosphoryl nitride (*phosphomonamide*) PON is obtained when phosphamide is heated to redness out of contact with air. Several phosphamic acids, and amides containing chlorine, are also known (*v.* Gladstone, Chem. Soc. Trans. 1864, 225 ; 1865, 1 ; 1866, 1 and 290 ; Salzmann, Ber. 1874, 7, 494 ; Winter, J. Amer. Chem. Soc. 1904, 26, 1484 ; Stokes, Amer. Chem. J. 19, 782).

Compounds of Phosphorus and Sulphur.

Several liquid and solid sulphides, all of which are very inflammable and more fusible than either of the constituent elements, are known. The liquids SP_4 and SP_2 are not compounds but only solutions of sulphur in phosphorus (Boulouch, Compt. rend. 1902, 135, 165 ; Stock and Bezhold, Ber. 1908, 41, 657 ; Stock, *ibid.* 1909, 42, 2062). The solid sulphides, P_4S_3, P_4S_7, and P_4S_{10} are obtained by carefully heating sulphur with amorphous phosphorus. The composition P_2S_6 (Dupré) or P_2S_{12} (Berzelius, Gmelin's Handb. 2, 218) has been assigned to a substance obtained in rhombic sulphur-like crystals by solution of sulphur in sulphur diphosphide. According to Ramme (Ber. 1879, 12, 940, 1350), the crystals are merely sulphur containing phosphorus (*cf.* Boulouch, Compt. rend. 1906, 143, 41).

Phosphorus pentasulphide P_4S_{10}, which is employed in the preparation of organic sulphur compounds, is produced by gently heating a mixture of excess of powdered roll sulphur and amorphous phosphorus. A small portion of the mixture is first heated in a stream of carbon dioxide until reaction sets in. The source of heat is then removed and the rest of the mixture is added in small quantities. After cooling, the mass is extracted with boiling carbon disulphide (Stock and Scharfenberg, Ber. 1908, 41, 558). The product forms a greyish-yellow crystalline mass, which may be obtained in transparent crystals by sublimation. According to Stock and Thiel (Ber. 1905, 38, 2719), the pentasulphide exists in at least two modifications. The ordinary compound melts at 274°–276° (Meyer, *ibid.* 1879, 12, 610), and boils at 519° at 734 mm. pressure (Goldschmidt, *ibid.* 1882, 15, 304). The other modification melts at about 255°, is more soluble in carbon disulphide and can be obtained by the distillation of the ordinary sulphide *in vacuô* and rapidly cooling the product (Stock and Scharfenberg, *l.c.*).

Phosphorus pentasulphide dissolves in liquid ammonia forming ammonia thioiminophosphate compounds from which iminothiophosphoric acid has been obtained (Stock, Ber. 1906, 39, 1967).

Phosphorus heptasulphide P_4S_7 forms rhombic prisms, m.p. 166°, b.p. 380°. It is easily inflammable and is slowly decomposed by boiling water forming hydrogen sulphide, phosphine, and phosphorous acid (Clayton, Chem. Soc. Proc. 1902, 129 ; *ibid.* 1903, 231 ; Mai and Scheffer, Ber. 1903, 36, 870 ; Mai, Ber. 1911, 44, 1229, *ibid.* 1725. To prepare P_4S_7 a cold saturated solution of 3 grams of phosphorus and 5·2 grams of sulphur in carbon disulphide is added to 20 grams of naphthalene heated to 110° ; the temperature is gradually raised to 195°. The sulphide crystallises out on cooling and is purified by extraction of the naphthalene with carbon disulphide, benzene, and light petroleum successively. The pentasulphide P_4S_{10} may be prepared similarly, using 4 grams of phosphorus, 13 grams of sulphur, and 35 grams of naphthalene.

In carbon disulphide solution, phosphorus heptasulphide absorbs iodine forming $P_4S_3I_2$, orange-yellow crystals, m.p. 119·5°—this compound can be used as a means of detecting the heptasulphide (Walter, Chem. Zeit. 1907, 31, 640). According to Gartenmeister (J. Soc. Chem. Ind. 1908, 837), easily inflammable but not explosive substances, which are not sensitive to moisture, can be obtained by heating together various proportions of red phosphorus, sulphur, and the sulphides of metals, such as antimony, to about 170°.

Phosphorus sulphoxides $P_4O_6S_4$, m.p. 102°, b.p. 295°, and $P_2O_2S_3$, which decomposes at 200°, forming phosphorus pentoxide and pentasulphide, have been prepared by Thorpe and Tutton (Chem. Soc. Trans. 1891, 1024), and Besson (Compt. rend. 1897, 124, 151). $P_4S_3O_4$ is a yellowish-white, amorphous powder, D=1·96 melting at 250° to a golden-yellow liquid, obtained by passing dry air or ozone through a solution of tetraphosphorus trisulphide P_4S_3 in carbon disulphide (Stock and Friederici, Ber. 1913, 46, 1380).

For other work on phosphorus sulphides, *v.* Rebs (Annalen, 1888, 246, 356), Dervin (Bull. Soc. chim. 41, 433), Isambert (Compt. rend. 1883, 96, 1499, 1771), Lemoine (*ibid.* 1630), Schulze (Ber. 1883, 16, 2066), Frouin (Chem. Zeit. Rep. 1899, 23, 213), Weelwright (J. Soc.

Chem. Ind. 1903, 229), Boulouch (Compt. rend. 1904, 138, 363 ; 1906, 142, 1045 ; 143, 41), Dervin (*ibid.* 138, 366), Girvan (*ibid.* 142, 398), Stock (Ber. 1909, 42, 2062), Mai (Ber. 1911, 44, 1229).

Compounds of Phosphorus and Selenium.

Phosphorus and selenium can be fused together in all proportions, a red mass being formed ; the only definite compounds, however, are P_4Se_3, P_2Se_5, and possibly P_2Se_3. These compounds are decomposed by moist air, and when treated with alkalis or alkali sulphides yield complex salts such as potassium thioselenophosphite $2K_2S,P_2Se_3,5H_2O$ (*v.* Berzelius, Gmelin's Handb. 2, 242 ; Bogen, Annalen, 1862, 124, 57 ; Hahn, J. pr. Chem. [i.] 93, 430 ; Muthmann and Clever, Zeitsch. anorg. Chem. 1896, 13, 191 ; Meyer, *ibid.* 1902, 30, 258).

Haloid compounds of Phosphorus.

Phosphorus trichloride PCl_3, may be prepared by passing dry chlorine over heated amorphous phosphorus, or over dry ordinary phosphorus, and digesting the product with ordinary phosphorus for some weeks to convert any pentachloride which may have been formed into the trichloride (Dumas, Ann. Chim. [iii.] 55, 172). Or, better, by leading a current of chlorine into boiling phosphorus chloride covering a quantity of red phosphorus. Formation of the pentachloride is not observed so long as any red phosphorus is uncombined. The process may be made continuous by distilling off the trichloride and adding fresh quantities of amorphous phosphorus. Phosphorus trichloride is a mobile, colourless, fuming liquid of pungent smell, boiling at 75·95° (760 mm.), and having a sp.gr. of $1{\cdot}61275\ \frac{0°}{4°}$ (Thorpe, Proc. Roy. Soc. 24, 295). It absorbs water with production of hydrochloric and phosphorous acids and a small quantity of phosphorus oxychloride, $POCl_3$ (Besson, Compt. rend. 1898, 125, 771). It dissolves phosphorus, and is itself soluble in benzene and carbon disulphide. When mixed with an aliphatic alcohol, heat is evolved, with production of the normal ester of phosphorous acid which is decomposed by the liberated hydrogen chloride into acid ester and alkyl chloride

$$PCl_3+3R{\cdot}OH=P(OR)_3+3HCl\rightarrow OH{\cdot}P(OR)_2 +RCl\rightarrow OR{\cdot}P(OH)_2\rightarrow P(OH)_3+RCl$$

(Béchamp. Compt. rend. 1855, 40, 944 ; 41, 23 ; Milobendzki and Sachnowski, Chem. Soc. Abt. 1918, i. 477). The decomposition of alkyl phosphites into phosphorous acid and unsaturated hydrocarbons is a secondary reaction which occurs most readily with esters derived from tertiary alcohols. It also unites with ammonia, forming additive compounds (Besson, *ibid.* 1890, 111, 972). With chromyl dichloride it reacts thus :

$$3PCl_3+2CrO_2Cl_2=2(CrOCl{\cdot}POCl_3)+PCl_5$$

The product is solid and extremely deliquescent and is decomposed by water thus :

$$CrOCl,POCl_3+2H_2O=CrCl_3+HCl+H_3PO_4$$

(Fry and Donnelly, J. Amer. Chem. Soc. 1916, 38, 1923).

Phosphorus trichloride reacts with glycerol and with glycol, yielding in the former case phosphorous esters of glycerol and of monochlorhydrin which are decomposed by water forming the compounds $P_2(OH)_4O_2{\cdot}C_3H_5OH$ and $P(OH)_2O{\cdot}C_3H_5OHCl$ of which the calcium derivatives have been isolated (Carré, Compt. rend. 1903, 136, 1456). With acetic acid it reacts according to the equation

$$3CH_3{\cdot}CO_2H+2PCl_3\rightarrow 3CH_3{\cdot}COCl+P(OH)_3$$

with simultaneous formation of small quantities of acetic anhydride, and *acetylphosphorous acid* $P(OH)_2{\cdot}OAc$ (Brooke, J. Amer. Chem. Soc. 1912, 34, 492).

Phosphorus pentachloride PCl_5 may be obtained by passing dry chlorine over the well-cooled trichloride until the whole is dry, or by the action of excess of chlorine on phosphorus. It is claimed (Fr. Pat. 463497) that calcium phosphate and sodium or potassium chloride heated together in a closed vessel at 1100° yield phosphorus pentachloride, lime, and potassium oxide :

$$Ca_3P_2O_8+10KCl=3CaO+5K_2O+2PCl_5$$

On the large scale, it is best prepared by passing excess of dry chlorine through a cooled solution of phosphorus in carbon disulphide, and finally crystallising out the product. It forms white lustrous crystals of unpleasant smell, volatilising below 100° without liquefying. Under pressure, it melts at 148° (Strecker). The vapour decomposes, when heated, into the trichloride and chlorine (Wanklyn and Robinson, Proc. Roy. Soc. 12, 507 ; Wegscheider, Monatsh. 1899, 20, 307). The dissociation may be represented by $\log p_1/p_2p_3=(21798/4{\cdot}571T)-11{\cdot}50$ where p_1 is the partial pressure of the pentachloride, p_2 and p_3 those of trichloride and chlorine respectively. The heat of dissociation under constant pressure is 21,800 cals. (Holland, Zeitsch. Elektrochem. 1912, 18, 234 ; *cf.* Smith and Calvert, J. Amer. Chem. Soc. 1914, 36, 1363). Nernst (Zeitsch. Elektrochem. 1916, 22, 37) calculates that Holland's results are best represented by $K_p=20{,}000/4{\cdot}57T-1{\cdot}75\log T-3{\cdot}78$ for temperatures between 413° and 623°.

In moist air, the pentachloride is converted into the oxychloride with evolution of hydrochloric acid. Sulphur trioxide converts it into the oxychloride with production of sulphuryl chloride : $SO_3+PCl_5=SO_2Cl_2+POCl_3$. Phosphorus pentachloride is much used in the preparation of organic chlorides. It forms chloramino derivatives or an additive compound with ammonia, depending on the temperature of the reaction (Besson, Compt. rend. *l.c.*).

Both chlorides form additive compounds with certain chlorides and bromides such as $PCl_3,2BBr_3$; $PCl_5,2BBr_3$, &c. (Tarible, Compt. rend. 1901, 132, 83 ; Strecker and Schuringin, Ber. 1909, 42, 1767).

Phosphorus dichloride P_2Cl_4 is a colourless oily liquid, fuming strongly, b.p. 180°, m.p. −28°, formed by submitting a mixture of phosphorus trichloride and hydrogen to the electric discharge (Besson and Fournier, Compt. rend. 1910, 150, 102).

Phosphorus chlorobromide PCl_3Br_2 is obtained by the action of bromine on phosphorus trichloride. It solidifies at −20°, and decomposes when heated to 35° (Michaelis, Ber. 1872,

5, 9). It combines with various proportions of bromine (*v.* Michaelis, *l.c.*; Prinvault, Compt. rend. 1872, 74, 868; and Stern, Chem. Soc. Trans. 1886, 815).

Phosphorus chloro-iodide PCl_3I_2 is said to be obtained in fine red hexagonal crystals by the action of iodine on phosphorus trichloride (Moot, Ber. 1879, 13, 2029).

Phosphoryl chloride (*phosphorus oxychloride*) $POCl_3$ may be prepared by heating dry oxalic or boric acid with the pentachloride:

$$PCl_3+H_2C_2O_4=POCl_3+2HCl+CO_2+CO$$

or by heating the pentachloride with the pentoxide in a sealed tube: $3PCl_5+P_2O_5=5POCl_3$. It can be conveniently prepared by the action of potassium chlorate on phosphorus trichloride (Dervin, Compt. rend. 1883, 97, 576; Ullmann and Fornaro, Ber. 1901, 34, 2172); or, according to Erdmann (Zeitsch. angew. Chem. 1903, 89), by passing a current of dry chlorine over a strongly heated, powdered mixture of carbon and a metaphosphate.

Phosphoryl chloride is a colourless, fuming liquid, boiling at 107·23° (760 mm.), and having a sp.gr. of $1·71163\frac{0°}{4°}$ (Thorpe, Chem. Soc. Trans. 37, 338). When cooled it solidifies to crystals which melt at −1·5° (Geuther and Michaelis, Ber. 1871, 4, 769). Its molecular depression of the freezing-point is 0·48° (Huntley, Chem. Soc. Trans. 1891, 205). Water rapidly decomposes it into hydrochloric and phosphoric acids. It forms crystalline double compounds with many metallic chlorides.

For its interaction with metallic oxides, *see* Bassett and Taylor (Chem. Soc. Trans. 1911, 99, 1402). For its action on methyl or ethyl alcohol, *see* Balareff (Zeitsch. anorg. Chem. 1917, 101, 225).

Metaphosphoryl chloride PO_2Cl (?). A straw-coloured viscous body obtained, together with phosphoryl chloride, by the action of chlorine on cooled phosphorous oxide (Thorpe and Tutton, Chem. Soc. Trans. 1890, 572), has been found to possess a composition corresponding with the formula PO_2Cl. It has, however, been shown by Huntley (*ibid.* 1891, 202) that this body consists of at least two substances, one of which is pyrophosphoryl chloride, whilst the other is a compound or mixture of the composition $P_7O_{15}Cl_5$.

According to Besson (Compt. rend. 1897, 124, 1099), metaphosphoryl chloride is obtained by the action of a small amount of water on phosphoryl chloride.

Pyrophosphoryl chloride $P_2O_3Cl_4$ is a colourless, fuming liquid, boiling between 210°–215°. It is obtained by the action of nitrogen peroxide on cooled phosphorus trichloride. Nitrosyl chloride is evolved, and pyrophosphoryl chloride remains, together with phosphorus pentoxide, phosphorus trichloride, and phosphoryl chloride, from which it is separated by fractional distillation (Geuther and Michaelis, Ber. 1871, 4, 767). It is also obtained, as stated above, or by the action of water on phosphorus pentachloride, or by treating the pentachloride (6 parts) with the pentoxide (1 part) (Oddo, Gazz. chim. ital. 1899, [ii.] 29, 330).

Phosphoryl bromodichloride $POBrCl_2$ (*v.* Menschutkin, J. pr. Chem. [i.] 98, 485; Besson, Compt. rend. 1896, 122, 814) is a highly refractive liquid, boiling at 135°–138° (760 mm.), and having a sp.gr. of $2·12065\frac{0°}{4°}$ (Thorpe, Chem. Soc. Trans. 37, 344). When cooled, it solidifies in tables, which melt at 11° (Geuther and Michaelis, Ber. 1871, 4, 769); at 13° (Besson, *l.c.*).

By the action of hydrogen bromide on phosphoryl chloride at 400°–500°, it is obtained together with *phosphoryl dibromochloride* $POBr_2Cl$, which melts at 30° and has b.p. 165° (Besson, *l.c.*).

Thiophosphoryl chloride $PSCl_3$ is a colourless, fuming liquid, produced by the action of hydrogen sulphide on the pentachloride, or, better, by heating a mixture of phosphorus pentasulphide and pentachloride. It boils at 125° (760 mm.), and has a sp.gr. of $1·6682\frac{40°}{0°}$ (Thorpe, Chem. Soc. Trans. 37, 341).

Nitrogen chlorophosphide $PNCl_2$ is obtained by gently heating a mixture of phosphorus pentachloride and mercurammonium chloride (white precipitate) or ammonium chloride (Stokes, Ber. 1895, 28, 437; Amer. Chem. J. 1896, 18, 629, 780; *ibid.* 1897, 19, 782; *ibid.* 1898, 20, 740; Besson, Compt. rend. 1892, 114, 1264, 1479; Besson and Rossett, *ibid.* 1906, 143, 37). It sublimes in rhombic prisms, melting at 110°, and boiling at 240° (*v.* Gladstone and Holmes, Chem. Soc. Trans. 17, 225).

With liquid ammonia, nitrogen chlorophosphide reacts thus:

$$PNCl_2+4NH_3=2NH_4Cl+PN(NH_2)_2$$

The compound PN_3H_4 is a white substance soluble in water, and on heating to 222° loses ammonia and is converted into phospham. Nitrogen chlorophosphide in carbon tetrachloride solution, when treated with dry ammonia gas, yields slender silky needles of the compound, $P_2N_3H_2Cl_3$, together with some PN_3H_4 (Besson, Compt. rend. 1908, 146, 1149).

A number of nitrogen chlorophosphides, all corresponding with the empirical formula $(PNCl_2)x$ have been obtained.

Phosphorus tribromide PBr_3 is best prepared by slowly dropping bromine on to excess of amorphous phosphorus in a flask fitted with an inverted condenser, or by dropping bromine on to ordinary phosphorus covered by a layer of benzene (Christomanos, Ber. 1904, 37, 2883). The rectified product is a colourless mobile liquid of strong, pungent smell, boiling at 172·9° (760 mm.), 170·8° (Christomanos), solidifying at −41·5°, and having a sp.gr. of $2·923\frac{0°}{4°}$ (Thorpe, Chem. Soc. Trans. 37, 335). It acts as a reducing agent on many organic compounds, and forms double salts of the type $CuBr_3,PBr_3$ (Arbusoff, J. Russ. Phys. Chem. Soc. 1906, 38, 293).

Phosphorus pentabromide PBr_5 is produced by the addition of bromine to the cooled tribromide; it forms yellow crystals of pungent smell, melting to a red liquid, which decomposes into the tribromide and bromine at 100°. According to Castle and Beaty (Amer. Chem. J. 1899, 21, 322; *ibid.* 1900, 23, 505), when the pentabromide is mixed with bromine and sublimed, red prisms of a *heptabromide*, PBr_7, are formed.

Phosphorus trifluorodibromide PF_3Br_2 has also been obtained.

Phosphoryl bromide (*phosphorus oxybromide*) $POBr_3$ occurs in flat tables, melting at 45°–46° and boiling at 195° (Ritter, J. 8, 301), and is prepared similarly to phosphoryl chloride.

According to Berger (Compt. rend. 1908, 146, 400), it forms colourless crystals, m.p. 55°–56°, b.p. 189·5° (774 mm.).

Phosphonium bromide PH_4Br crystallises in colourless cubes, b.p. 30° and resembles the iodine compound.

Thiophosphoryl bromide $PSBr_3$, a yellow, crystalline body, m.p. 38°, *pyrothiophosphoryl bromide* $P_2S_3Br_4$, a fuming yellow oily liquid, and *metathiophosphoryl bromide* PS_2Br, are also known.

Bromo-chloro-thio compounds of phosphorus have been prepared by Besson (Compt. rend. 1896, 122, 1057).

Phosphorus di-iodide P_2I_4 is prepared by the gradual addition of 8·2 parts of iodine to a solution of 1 part of phosphorus in carbon disulphide. On distilling off the disulphide, or on cooling it, the iodide remains or crystallises out in bright orange-yellow crystals which fuse at about 110° (Corenwinder, Ann. Chim. [iii.] 30, 242).

A rapid and safe method of producing phosphorus di-iodide is described by Doughty (J. Amer. Chem. Soc. 1905, 27, 1444); 50 grams of iodine and 4 grams of red phosphorus are heated in a 200 c.c. flask over a free flame until melted. After cooling to 60°, 2·5 grams of yellow phosphorus are added in small pieces.

When dry iodine is added to a solution of phosphorus in dry carbon disulphide, in quantity less than that necessary to convert the phosphorus into the di-iodide and the mixture is exposed to sunlight, *phosphorus subiodide*, P_4I, separates.

It is an amorphous, red powder which decomposes without melting and is decomposed by most reagents (Boulough, Compt. rend. 1905, 141, 256).

Phosphorus tri-iodide PI_3 is prepared similarly to the di-iodide, but with the use of a correspondingly larger proportion of iodine. It forms red six-sided deliquescent prisms, m.p. 61° (Corenwinder, *l.c.*, Snape, Chem. News. 1896, 74, 27; Besson, Compt. rend. 1897, 124, 1346).

Phosphonium iodide PH_4I is obtained by the union of phosphine with hydriodic acid, or by the action of water and iodine on excess of phosphorus. The iodine and phosphorus are preferably combined in carbon disulphide, which is then distilled off and the water added gradually during passage of carbon dioxide (Hofmann, Ber. 1873, 6, 291). The iodide is thus obtained as a sublimate of glistening deliquescent quadratic prisms, b.p. about 80° but readily vapourising at a lower temperature, decomposed by water into hydriodic acid and phosphine. It is a powerful reducing agent, and is employed as such in the preparation of many organic compounds. For its crystal structure, see Dickinson, J. Amer. Chem. Soc. 1922, 44, 1489.

Phosphorus thioiodide, P_2SI_2, m.p. 75° (Besson, Compt. rend. 1896, 122, 1057), and P_2S_3I (Ouvrard, *ibid.* 1892, 115, 1301) also exist.

Phosphorus trifluoride PF_3 may be prepared by carefully heating dry copper phosphide with lead fluoride, or by allowing arsenic trifluoride to drop upon phosphorus trichloride, or, preferably, by gently warming a mixture of dry zinc fluoride and phosphorus tribromide. It is a colourless, sharp-smelling gas, which condenses at −10° under a pressure of 40 atmospheres to a colourless mobile liquid, b.p. −95°, and solidifying at −160°. The gas dissolves slowly in water. It produces silicon fluoride, with separation of phosphorus, when heated in contact with glass. It combines directly with bromine, giving an amber-coloured mobile liquid having the composition PF_3Br_2 (Moissan, Compt. rend. 1884, 99, 655, 970; 1885, 100, 272, 1348; Ann. Chim. [vi.] 19, 286).

Phosphorus pentafluoride PF_5 is obtained by the action of arsenic trifluoride on phosphorus pentachloride (Thorpe, Proc. Roy. Soc. 1876, 122). It is a heavy, fuming, colourless, uninflammable gas, which is rapidly decomposed by water into hydrofluoric acid and phosphoric acid. It combines with dry ammonia to produce a white solid $2PF_5 \cdot 5NH_3$, and, according to Tassel (Compt. rend. 1890, 110, 1264), combines with nitrogen peroxide to produce a white crystalline compound of the composition $PF_5 \cdot NO_2$; *v.* also Moissan (*ibid.* 1885, 101, 1490; 1886, 103, 1257). It condenses to a liquid, b.p. −75° and solidifies to a flocculent mass at −83° (Moissan, *ibid.* 1904, 138, 789).

Phosphoryl fluoride, phosphorus oxyfluoride POF_3 may be prepared by the action of the electric spark on a mixture of phosphorus trifluoride and oxygen, by the action of phosphorus oxychloride on gently warmed zinc fluoride (Moissan, Compt. rend. 1886, 102, 1245; Bull. Soc. chim. 1891, [iii.] 5, 458), or, better, by the method employed by Thorpe and Hambly (Chem Soc. Trans. 1889, 759), which consists in gently heating a mixture of cryolite and phosphorus pentoxide. It is a colourless, fuming gas, rapidly absorbed by water, and without action, when dry, on glass or mercury. It condenses to a liquid which boils at −40° and solidifies to a crystalline mass at −68° (Moissan, *l.c.*).

Thiophosphoryl fluoride PSF_3 may be obtained by heating a mixture of arsenic trifluoride and phosphorus thiochloride in a sealed glass tube to 150°, or by heating a mixture of amorphous phosphorus, sulphur, and lead or bismuth fluoride, or, preferably, by heating a mixture of powdered, freshly-fused lead fluoride, and freshly-made phosphorus pentasulphide in a leaden tube from which air has been expelled by a current of dry nitrogen: $P_2S_5 + 3PbF_2 = 3PbS + 2PSF_3$. The action commences at 170°, and the temperature should be kept below 250°. The gas is stored over mercury in a glass holder containing fragments of quicklime, which gradually absorb the phosphorus trifluoride and any trace of silicon fluoride contained in the gas. The quicklime should be freed from air before use by repeatedly passing dry nitrogen into the holder and exhausting with a Sprengel pump. At ordinary temperatures, thiophosphoryl fluoride is a heavy colourless gas which condenses at a pressure of 10 to 11 atmospheres to a colourless liquid. A jet of the gas burns spontaneously with a greyish-green flame of extremely low heating power. If a considerable quantity of the gas be suddenly exposed to the air, a fine blue flash, followed by the greyish-green flame, is observed. The gas burns spontaneously with a yellow flame in

oxygen, but the dry gas does not inflame in dry oxygen in presence of a sufficiency of its oxidation products. The mixture instantly inflames on exposure to air or on introduction of moisture.

When heated or exposed to the electric spark, the gas is decomposed into sulphur, phosphorus, and phosphorus fluorides. It is without action on mercury, sulphuric acid, carbon disulphide, or benzene. It dissolves to some extent in ether, the solution burning with a greenish flame. It dissolves slowly with decomposition in water and solution of potash, soda, or ammonia. It combines with ammonia gas to form a white solid. Gently heated sodium burns with a red flame in the gas, the residue evolving spontaneously inflammable phosphine when treated with water. When heated in a glass tube the gas deposits phosphorus and sulphur, with formation of silicon tetrafluoride, which occupies three-fourths of the volume of the original gas: $4PSF_3+3Si=3SiF_4+P_4+S_4$ (Thorpe and Rodger, Chem. Soc. Trans. 1888, 766; 1889, 306).

Oxides and acids of Phosphorus.

The product of the combustion of phosphorus in a limited supply of air consists of a mixture of the four oxides P_4O, P_4O_6, P_2O_4, and P_4O_{10}.

The first of these oxides, P_4O, was obtained by Le Verrier (Annalen, 1838, 27, 167), but whilst its existence has been maintained by some chemists, it is denied by many others (Michaelis and Pitsch, *ibid.* 1899, 310, 45; Michaelis and Arend, *ibid.* 1900, 314, 259; 1902, 325, 361; Biltz, Ber. 1894, 27, 1257; Besson, Compt. rend. 1897, 124, 763; 1897, 125, 1032; 1901, 132, 1556; Chapman and Libury, Chem. Soc. Trans. 1899, 973; Burgess and Chapman, *ibid.* 1901, 1235; Browning, Chem. Soc. Proc. 1901, 243; Jungfleisch, Compt. rend. 1907, 145, 325).

Phosphorous oxide, phosphorous anhydride P_4O_6. The existence of this compound as one of the products of the slow combustion of phosphorus seems to have been first noticed by Sage in 1777. It appears also to have been obtained by Cabell as a sublimate from the mixed oxides (Chem. News, 50, 209). It, however, received no systematic examination until Thorpe and Tutton (Chem. Soc. Trans. 1890, 545; 1891, 1019) obtained it in a state of purity by the following method:—

Pieces of dried phosphorus are placed in a glass tube drawn out, but open at one end, and connected at the other end with a brass tube surrounded by a tube filled with water. The inner tube is connected with a long-limbed U-tube fitted at the bend with a branch leading to a small bottle, into which the product of the action may be passed by warming the limbs of the U-tube. A freezing mixture surrounds the U-tube and bottle.

The phosphorus having been ignited by heating the tube, is oxidised by drawing air through the apparatus with an aspirator, and after about 15 minutes, the water around the brass tube is heated to about 50°, as indicated by a thermometer fitted to the outer tube, and the temperature is maintained thereabouts until near the end of the operation, when it is raised to about 60°. The readily fusible trioxide gradually passes over from the combustion products in the brass tube and solidifies in the U-tube, a loose plug of glass wool in the brass tube preventing passage of the other oxides. The action is stopped when about four-fifths of the phosphorus has been burned, in order to diminish the chance of oxidising the product.

The product solidifies in the U-tube as a snow-white waxy mass. It may also be obtained in long feathery aggregations or in thin isolated prisms, terminated by pyramids, and probably belonging to the monoclinic system, as do those of the corresponding compound with arsenic or antimony.

According to Jungfleisch (*l.c.*), a continuous yield of well-defined crystals of phosphorous oxide can be obtained by oxidising pure dry phosphorus at a low temperature at 18–20 mm. pressure.

Phosphorous oxide possesses a peculiar phosphorus-like smell. It fuses at 22·5° to a mobile liquid, sp.gr. 1·9358 $\frac{24\cdot8^\circ}{4^\circ}$, which normally resolidifies at 21°, but which sometimes exhibits the property of superfusion. It boils at 173·1° (760 mm.). When heated in a sealed tube to about 210° the oxide becomes turbid, and at 440° is entirely decomposed into the tetroxide and amorphous phosphorus.

Phosphorous oxide is slowly dissolved by cold water, forming phosphorous acid. With hot water the action is violent, large quantities of the red suboxide, or amorphous phosphorus, being produced, with evolution of spontaneously inflammable phosphine.

Phosphorous oxide dissolves unchanged in ether, carbon disulphide, benzene, or chloroform, but is instantly ignited in contact with absolute alcohol. When this action is properly controlled, *di-ethyl phosphorous acid* is obtained.

The oxide is spontaneously oxidised in presence of air or oxygen. When thrown into oxygen heated at 50° or 60°, it ignites with great brilliancy. It inflames readily when exposed to the air, especially when warmed or when in contact with fabrics or paper. For conditions determining the luminescence and ionisation in the oxidation of phosphorous oxide, *see* Rinde (Arkw. Kern. Min. Geol. 1917–18, 7, No. 7, 1; in abstract, Chem. Soc. Abst. 1920, ii. 108). When thrown into chlorine, it burns with a greenish flame. The slow action of chlorine on the cooled oxide gives a mixture of phosphoryl chloride and the so-called metaphosphoryl chloride.

Bromine acts in a similar manner, but with previous formation of phosphorus pentabromide. With iodine it forms the tetraiodide and the pentoxide: $5P_4O_6+8I_2=4P_2I_4+6P_2O_5$. Heated with sulphur it yields *phosphorus sulphoxide* $P_4O_6S_4$, forming clear transparent crystals, m.p. 102° and b.p. 295°, deliquescing rapidly in the air, and readily dissolved by water, forming sulphuretted hydrogen and phosphoric acid: $P_4O_6S_4+10H_2O=4H_3PO_4+4H_2S$ (Thorpe and Tutton, Chem. Soc. Trans. 1891, 1023).

Vapour density determinations show that the gaseous molecule of the oxide has the formula P_4O_6. Determinations of the molecular weight by Raoult's method give similar results.

Phosphorus tetroxide P_2O_4 was first obtained by Thorpe and Tutton (Chem. Soc. Trans. 1886, 833) by heating the mixed oxides obtained by

the slow combustion of phosphorus in a sealed exhausted tube at about 290°. A sublimate of this oxide in clear, transparent, lustrous, colourless, orthorhombic crystals of sp.gr. 2·537 at 22·6/4°, volatilising at about 180°, is thus obtained. It may be prepared, together with amorphous phosphorus, by heating phosphorous oxide in a sealed tube to about 440°.

This oxide is highly deliquescent and dissolves in water, with evolution of heat, the strongly acid solution being unchanged on boiling. The solution reduces mercuric chloride to calomel on warming, and gives a white precipitate, which rapidly blackens with silver nitrate. Its vapour density at 1400° is 230 (West, Chem. Soc. Trans. 1902, 933).

Phosphorus pentoxide, phosphoric oxide, phosphoric anhydride P_4O_{10} is the product of the complete combustion of phosphorus. It may be obtained in a state of purity by suspending a porcelain dish, containing burning phosphorus, in a three-necked globe, and drawing dried air through the globe with an aspirator. Two of the necks serve for the entrance and exit of the air, and the third and vertical neck receives a corked tube, through which pieces of dried phosphorus are dropped at intervals into the dish.

Grabowski (Annalen, 1865, 136, 119) recommends for the preparation on the large scale the use of a sheet-iron cylinder, having a cover and resting on a sheet-iron funnel. The cover has a chimney closed by a cork, and a damper is fitted to the apparatus so that the air may be admitted as required. The oxide produced is shaken at intervals into a bottle beneath the funnel.

This oxide is a white amorphous powder which, when pure, is perfectly colourless and odourless. It frequently possesses a garlic smell, from the presence of phosphorous oxide, and may have a yellowish colour, more noticeable when a portion is allowed to deliquesce, from presence of the lower oxide P_4O or of red phosphorus. To free the oxide from all traces of lower oxides, it should be distilled over platinum sponge in a current of oxygen, until the product no longer reduces silver nitrate solution (Threlfall, Phil. Mag. 1893, [v.] 35, 14; Shenstone and Beck, Chem. Soc. Trans. 1893, 473). It rapidly deliquesces, with production of metaphosphoric acid. When added to water, orthophosphoric acid is gradually produced, with evolution of heat. According to Hautefeuille and Perrey (Compt. rend. 1884, 99, 33), it exists in three forms, crystalline, pulverulent and vitreous (Giran, *ibid.* 1903, 136, 550).

Phosphorus pentoxide is the best desiccating agent known, and is largely used in the laboratory for completing the desiccation of gases and liquids, or for removing the elements of water from compounds, as in the preparation of nitrogen pentoxide. Phosphorus pentoxide, when completely pure is capable of becoming highly phosphorescent *in vacuô* (Ebert and Hoffmann, Zeitsch. physikal. Chem. 1900, 80).

According to Besson (Compt. rend. 1897, 124, 763), the oxide P_2O also exists.

Hypophosphorous acid H_3PO_2 is a monobasic acid the salts of which are formed when alkalis or alkaline earths are boiled with phosphorus. The barium salt $Ba(PH_2O_2)_2$ is of most interest, as the acid and salts are usually prepared from it. This salt is formed, with evolution of phosphoretted hydrogen, on boiling phosphorus with baryta water:—$3Ba(OH)_2+2P_4+6H_2O=3Ba(PH_2O_2)_2+2PH_3$. It may be decomposed by dilute sulphuric acid to obtain the acid, or by the addition of a sulphate to produce another hypophosphite (Marie, Compt. rend. 1904, 138, 1216).

Hypophosphorous acid forms a thick syrup, from which crystals melting at 26·5° (Marie) may be obtained by evaporation below the boiling-point of the solution, and cooling in a freezing mixture. When strongly heated, it decomposes into phosphoretted hydrogen and phosphoric acid. It reduces mercuric chloride to calomel or mercury (Sieverts, Zeitsch. anorg. Chem. 1909, 64, 29), and is oxidised to phosphoric acid by chlorine and other oxidising agents (Steele, Chem. Soc. Proc. 1908, 193; Mitchell, Chem. Soc. Trans. 1920, 117, 1322). When concentrated it attacks glass and porcelain more readily than phosphoric acid. Most hypophosphites dissolve in water, and many in alcohol. They are all powerful reducing agents, and precipitate gold and silver from solution. The sodium salt is used in medicine. For the preparation of hypophosphites, compare Kendal (J. Soc. Chem. Ind. 1890, 1129).

According to Mai (Ber. 1902, 35, 162), hypophosphorous acid reacts with organic diazo compounds forming hydrocarbons, this being in some cases an advantageous method of forming the latter. When boiled with acetone, hypophosphorous acid yields crystalline products, $H_3PO_2{\cdot}2C_3H_6O$; $H_3PO_2{\cdot}C_3H_6O$; and $H_3PO_3{\cdot}C_3H_6O$ (Marie, Compt. rend. 1901, 133, 219).

Hypophosphoric acid $H_4P_2O_6$, a tetrabasic acid forming two classes of salts, normal and acid. Formed together with phosphoric and phosphorous acids by the slow oxidation of phosphorus in moist air. According to Van Name and Huff (Amer. J. Sci. 1918, 46, 587) the sodium salt is best prepared by suspending a number of sticks of phosphorus cast round glass rods in a stout glass jar containing a litre of water and 250 grams of sodium carbonate. The sticks of phosphorus should be about $3\frac{1}{2}$ in. long and $\frac{2}{3}$ in. diameter, and should protrude about $\frac{1}{3}$ in. from the solution. The whole is then placed in a cool position (10°–15°) and left to react until a few drops of the solution just turn Congo red. The product sodium hydrogen hypophosphate, $H_2Na_2P_2O_6{,}9H_2O$, is found in part as a crystalline precipitate at the bottom of the jar, whilst the remainder is obtained by concentrating the solution. It is recrystallised to remove the accompanying phosphates and phosphites. A solution of this salt yields with lead acetate an insoluble salt $Pb_2P_2O_6$ which, suspended in water and treated with hydrogen sulphide, yields an odourless acid solution decomposing on concentration.

Phosphorous acid $P(OH)_3$ is obtained by the action of water on phosphorous oxide or of moist air on phosphorus. The pure acid may be prepared by the decomposition of phosphorus trichloride with water, or with concentrated hydrochloric acid, or by slowly passing chlorine through a deep layer of phosphorus melted under water—

$$PCl_3+3H_2O=P(OH)_3+3HCl$$

On evaporating the solution until it attains a temperature of 180° and forms a thick syrup, it gives on cooling a crystalline mass melting at 70·1° (Thomsen, Ber. 1874, 7, 996). When strongly heated, the acid produces phosphoretted hydrogen and phosphoric acid. The aqueous solution slowly absorbs oxygen. It is a powerful reducing agent, and precipitates gold, silver, and mercury from solution.

Phosphorous acid is tribasic, but, excepting the tribasic sodium salt and some ethereal salts, only two atoms of hydrogen are replaceable by the base. All phosphites are soluble in water, the normal alkaline salts being most soluble. They act as reducing agents similarly to the hypophosphites, but, unlike them, give a precipitate with lime water.

Pyrophosphorous acid $H_4P_2O_5$ is obtained by passing the vapour of phosphorus trichloride volatilised by a stream of carbon dioxide through the product of the reaction of water on an excess of the trichloride for 20 hours. It is then placed in a vacuum over fused potash and phosphorus pentoxide. It can also be obtained by the continuous agitation for about 5 hours at 30°–40° of a mixture of phosphorous acid and phosphorus trichloride. It melts at 38°, is readily decomposed by water, at 130° gives off phosphine and at 45° in presence of phosphorus trichloride yields phosphorus and phosphoric or pyrophosphoric acid (Auger, Compt. rend. 1903, 136, 814). The pyrophosphites, such as $Na_4P_2O_5$, also exist.

Phosphoric acids. Three acids, produced by the combination of phosphorus pentoxide with one, two, and three molecules of water respectively, are known, their names and composition being as follows: *Metaphosphoric acid* HPO_3 or $P_2O_5H_2O$; *pyrophosphoric acid* $H_4P_2O_7$ or $P_2O_52H_2O$; and *orthophosphoric acid* H_3PO_4 or $P_2O_53H_2O$. The sodium and silver salts of a fourth acid $P_4O_7(HO)_6$ or $2P_2O_5{\cdot}3H_2O$, which may be called tetraphosphoric acid, are also known (Fleitmann and Henneberg, Annalen, 1848, 65, 324). Salzer (*ibid.* 1877, 187, 322) has described a phosphoroso-phosphoric acid or hypophosphoric acid $P_4O_4(HO)_8$ of which phosphorus tetroxide may perhaps be the anhydride (Rosenheim and Pritze, Ber. 1908, 41, 2708). Finally, the sodium salt of *thiophosphoric acid* H_3PSO_3 (Wurtz, Ann. Chim. [iii.] 20, 472), and the salts of di- and tri- thiophosphoric acid, $H_3PS_2O_2$ and H_3PS_3O, are also known (Kubierschky, J. pr. Chem. 1885, [ii.] 31, 93).

Several series of thiophosphates have been prepared by heating the metals with phosphorus and sulphur (Ferrand, Bull. Soc. chim. 1895, [iii.] 13, 115; Compt. rend. 1896, 122, 886).

Orthophosphoric acid H_3PO_4, usually known as 'phosphoric acid,' is a tribasic acid which is produced when amorphous phosphorus is heated with concentrated nitric acid (Watson, J. Soc. Chem. Ind. 1892, 224). The phosphorus slowly dissolves, with evolution of red fumes, and the solution is evaporated in a dish with repeated additions of nitric acid until red fumes cease to be evolved, to ensure the absence of phosphorous acid.

The acid is prepared commercially from bone ash by digesting 3 parts of the ash with 3 parts of crude sulphuric acid (1·55) and 18 or 20 parts of water for two or three days. The solution, which contains the phosphorus as calcium tetrahydric diphosphate ('superphosphate of lime'), is then pressed in linen filters from the precipitated calcium sulphate, and is concentrated to a syrup, treated with strong sulphuric acid to precipitate the lime, and the solution filtered off, evaporated, and heated to remove the sulphuric acid. By another process the solution is treated with ammonium carbonate, which precipitates the lime and leaves triammonium phosphate in solution. The solution is separated and evaporated, and heated to expel the ammonia. The acid obtained by either method contains magnesia and other impurities.

In another process the bone ash is dissolved in its own weight of hydrochloric acid of sp.gr. 1·18, diluted with 4 parts of water and 1½ parts of sodium sulphate is added. The filtered solution is neutralised while hot with sodium carbonate, refiltered, and precipitated with barium chloride. The mixture of barium sulphate and phosphate thus obtained is decomposed by sulphuric acid.

The bones, apatite or horn piths, &c., may be dried, ground, and digested with aqueous phosphoric acid, after which the product is treated with sulphuric acid (Lomas, J. Soc. Chem. Ind. 1900, 836; Eng. Pat. 9611).

According to Maywald (J. Soc. Chem. Ind. 1908, 1151), phosphoric acid may be manufactured by maintaining a low potential arc produced by a current of 60 volts, in a granular mass of phosphates to which air has access: the phosphoric acid is volatilised and collected.

Other manufacturing methods are described by Hatmaker (J. Soc. Chem. Ind. 1902, 1533; Powter, *ibid.* 1904, 252; Bandon, *ibid.* 1904, 787).

Commercial phosphoric acid frequently contains arsenic, derived either from the phosphorus used or from the acid employed in dissolving the bones, &c. The arsenic may be removed by reducing it to arsenious oxide with sulphurous acid, and precipitating it by sulphuretted hydrogen, after removing the excess of the sulphurous acid by boiling.

To avoid the necessity for removing the arsenic, Wenzell (Proc. Am. Pharm. Assoc. 1882, 556, and Pharm. J. [iii.] 14, 24) prepared the acid by the slow, spontaneous oxidation of phosphorus in trays containing a thin layer of water. The phosphorous acid thus produced contains the arsenic as arsenious oxide, which becomes reduced to the elemental state, so that it may be separated by filtration, when the solution is heated to about 190° for half an hour. The filtered solution is oxidised to phosphoric acid by the action of nitric acid (Runyon, Pharm. J. [iii.] 14, 48; Sommer, J. Soc. Chem. Ind. 1885, 574).

To prepare the pure acid the commercial acid may be precipitated as the lead salt by addition of lead acetate, the precipitate being washed and decomposed by subjecting it while suspended in water to the action of hydrogen sulphide, or by treating it with dilute sulphuric acid. In the latter case the solution must be evaporated and heated to remove sulphuric acid, and be then redissolved and freed from traces of lead by means of hydrogen sulphide.

Phosphoric acid for medicinal purposes is

also prepared by dissolving the pentoxide in water.

According to Nicolas (Compt. rend. 1890, 111, 974), pure phosphoric acid may be prepared by gradually adding pure calcium phosphate to a slight excess of pure dilute hydrofluoric acid contained in a lead or platinum vessel, the mixture being well stirred after each addition. The high temperature of the mixture is maintained for some time to complete the reaction; the calcium fluoride formed is removed by filtration and the filtrate, consisting of a solution of phosphoric acid, is evaporated until a thick syrup is obtained. By further evaporation meta- and pyrophosphoric acids can be obtained.

By evaporation of its solution *in vacuô* over sulphuric acid, orthophosphoric acid may be obtained in hard, transparent, deliquescent, six-sided orthorhombic prisms fusing at 38·6° and losing water at 160°. At about 215° the acid is converted into pyrophosphoric acid, and when heated until dense white fumes begin to be evolved is converted into a highly deliquescent glassy mass of metaphosphoric acid.

The strength of aqueous solutions at 15·5° is shown in the following table (J. Watts, Chem. News, 1865, 12, 160) :—

Specific gravity.	P_2O_5 in 100 parts	Specific gravity	P_2O_5 in 100 parts
1·508	49·60	1·247	28·24
1·492	48·41	1·236	27·30
1·476	47·10	1·226	26·30
1·464	45·63	1·211	24·79
1·453	45·38	1·197	23·23
1·442	44·13	1·185	22·07
1·434	43·95	1·173	20·91
1·426	43·28	1·162	19·73
1·418	42·61	1·153	18·81
1·401	41·60	1·144	17·89
1·392	40·86	1·136	16·95
1·384	40·12	1·124	15·64
1·376	39·66	1·113	14·33
1·369	39·21	1·109	13·25
1·356	38·00	1·095	12·18
1·349	37·37	1·081	10·44
1·339	36·74	1·073	9·53
1·328	36·15	1·066	8·62
1·315	34·82	1·056	7·39
1·302	33·49	1·047	6·17
1·293	32·71	1·031	4·15
1·285	31·94	1·022	3·03
1·276	31·03	1·014	1·91
1·268	30·13	1·006	0·79
1·257	29·16		

A simple method of determining the strength of phosphoric acid solutions employed in pharmacy is to transfer the solution to be tested into a graduated flask and to add an excess of N/1 ammonia solution followed by an excess of a saturated neutral solution of magnesium sulphate. The liquid is then diluted to the mark on the flask, well shaken and filtered, and the residual ammonia is then titrated in an aliquot part of the filtrate (Segalle, Zeitsch. anal. Chem. 1895, 33).

Phosphoric acid attacks glass, porcelain, and other silicates, also fused silica at a temperature above 300°, silicyl phosphate and phosphates of the bases being formed. It dissolves ferro-chromium alloys, ferro-silicon and spiegeleisen, but the silica of the latter remains undissolved (Byron, J. Soc. Chem. Ind. 1902, 214).

It is partially converted into the pyro-acid when kept in a desiccator over phosphoric oxide, or sulphuric acid.

When present in sufficient quantity, phosphoric acid increases the translucency and improves the colour of pottery bodies. It also acts as a flux and vitrifying agent (Parmelee, Trans. Amer. Ceramic Soc. 1906, 8, 236).

Both ortho- and pyro- phosphoric acids form a series of hydrates, those of the latter being less stable and readily passing into the ortho- condition (Giran, Compt. rend. 146, 1270; Smith and Menzies, J. Amer. Chem. Soc. 1909, 31, 1183).

Phosphoric acid possesses three degrees of basicity, the first that of a strong acid, the second that of a weak acid like acetic, the third that of an alcohol, and these correspond with the formation of mono-, di- and tribasic phosphates (Berthelot, Compt. rend. 132, 1277, 1517; Cavalier, *ibid.* 1330), of which the sodium salts may be taken as types. These include the normal or tri-sodium phosphate $Na_3PO_4,2H_2O$, the hydrogen disodium phosphate $HNa_2PO_4,12H_2O$, and the di-hydrogen sodium phosphate

$$H_2NaPO_4,H_2O$$

The normal alkaline salts are readily soluble and possess an alkaline reaction. The insoluble normal phosphates are converted by dilute acids, even by carbon dioxide, into the soluble hydrogen phosphates. Hydrogen disodium phosphate and corresponding salts are obtained by adding a solution of the hydroxide or carbonate of the base to phosphoric acid until weakly alkaline. The dihydrogen phosphates of the alkalis are soluble and slightly acid. When strongly heated they produce metaphosphates with evolution of water.

The phosphates, which can be freed from phosphoric acid by heating them in a current of chlorine and carbon tetrachloride (Jannasch and Jilke, J. pr. Chem. 1908, [ii.] 78, 21), are, according to Specht and Hutschek (Zeitsch. Farben and Textil. Ind. 1905, 4, 297), very effective as reserves in dyeing processes. This is particularly true of the alkali salts.

When glacial phosphoric acid is heated with glycerol to 100° and the product, after neutralising with barium carbonate and filtering, is decomposed with the calculated amount of sulphuric acid, *glycerophosphoric acid* is obtained (Porte and Prunier, J. Pharm. Chim. 1894, 393; Adrian and Trillat, *ibid.* 1898, [v.] 7, 226; Compt. rend. 1898, 126, 1215; Bull. Soc. chim. 1898, 19, 684; Imbert and Belugon, *ibid.* 21, 935; Carré, Compt. rend. 1901, 133, 182; 1903, 137, 1070; 1904, 138, 47; Contardi, Gazzetta, 1912, 42, ii. 270). Glycerophosphoric acid yields normal and acid salts with the metals and also combines with organic bases such as quinine, cocaine, &c. Phosphoric acid also reacts with mannitol (Carré, *ibid.* 1903, 136, 306).

Phosphoric acid esters can be prepared by stirring together a halogen or fatty acid derivative of a di-glyceride (2 mols.) with phosphorus

pentoxide (1 mol.) and water (1 mol.) (Ulzer and Batik, J. Soc. Chem. Ind. 1908, 713; D. R. P. 193189; Arbusoff, Ber. 1905, 38, 1171; Carré, Ann. Chim. 1905, [viii.] 5, 345; Young, Chem. Soc. Proc. 1907, 65).

Pyrophosphoric acid $H_4P_2O_7$ is obtained by heating orthophosphoric acid to 215° for some time (Giran, Compt. rend 1902, 134, 1499; 1902, 135, 961; Rosenheim and Pritze, *l.c.*). It occurs either as a soft glass or as an opaque crystalline mass; crystals separate from the syrupy acid at −10° and melt at 61° (Giran, *l.c.*). It may be obtained in solution by precipitating the sodium salt with lead acetate and decomposing the precipitate with hydrogen sulphide. When heated in solution it is converted into orthophosphoric acid (Berthelot and André, Compt. rend. 1896, 123, 776; 1897, 124, 265; Giran, Ann. Chim. 1903, [vii.] 30, 203; Tanatar, J. Russ. Phys. Chem. Soc. 1898, 30, 99; Balarew, Zeitsch. anorg. Chem. 1910, 68, 288; Holt and Myers, Chem. Soc. Trans. 1911, 99, 384; Montemartini and Egidi, Gazz. chim. ital. 1902, 32, i. 381).

Pyrophosphates are obtained by heating the mono-hydrogen phosphates, or by addition of the base to the acid. Both normal and acid sodium and other alkaline pyrophosphates, having an alkaline and an acid reaction respectively, are known. When heated with an acid they are converted into orthophosphates (Ridenour, Chem. Zentr. 1900, i. 834).

For the structure of pyrophosphoric acid and orthophosphoric acid, *see* Balarew, Zeitsch. anorg. Chem. 1914, 88, 133.

Pyrophosphoric acid may be recognised in the presence of orthophosphoric acid as follows: To 20 c.c. of the solution made slightly alkaline to phenolphthalein are added four or five drops of 5 p.c. copper sulphate solution and then, drop by drop, dilute acetic acid, until the precipitate formed is just redissolved. Then a small crystal of $Cu_2P_2O_7$ is dropped into the clear solution. In presence of pyrophosphoric acid, there is precipitated, either immediately or in a few hours, small pale grey crystals of copper pyrophosphate.

Another test is to add silver nitrate and then dilute acetic acid to the neutral solution under examination. The yellow orthophosphate goes into solution, leaving the white pyrophosphate. In the presence of both ortho- and metaphosphoric acids it is necessary to ascertain that the precipitate is not a metaphosphate by filtering it off, washing with very dilute acetic acid, dissolving in the minimum quantity of nitric acid, neutralising the solution, again acidifying with acetic acid, and treating with albumen solution. A precipitate indicates the presence of pyrophosphoric acid (Balarew, Zeitsch. anal. Chem. 1921, ii. 385).

Metaphosphoric acid HPO_3 is obtained as a transparent, highly deliquescent glassy mass when orthophosphoric acid is heated until dense white fumes begin to be evolved. It is then known as *glacial phosphoric acid*, and usually contains sodium phosphate, which communicates hardness to the otherwise soft acid (Brescius, Zeitsch. anal. Chem. 6, 187; Bettendorff, *ibid.* 27, 24).

It is also obtained by the spontaneous deliquescence of phosphorus pentoxide.

On standing at the ordinary temperature, or more rapidly when boiled, metaphosphoric acid is changed into the ordinary ortho- acid (Berthelot and André, Compt. rend. 1897, 124, 265; Montemartini and Egidi, Gazz. chim. ital. 1901, i. 31, 394).

Metaphosphoric acid volatilises at a bright red heat, and in the state of vapour has a molecular weight corresponding with the formula $(HPO_3)_2$. Its salts are prepared by neutralising the acid or by heating a dihydric orthophosphate. Among the salts no less than six modifications are known. They may be regarded as salts of polymeric metaphosphoric acids, and are respectively known as mono-, di-, tri-, tetra-, penta- and hexa-metaphosphates (*cf.* Holl and Myers, Chem. Soc. Trans. 1913, 103, 532).

Various esters, alkyl and other organic derivatives of phosphorus have been prepared (Giran, Compt. rend. 1898, 126, 592; Cavalier, *ibid.* 1898, 127, 60; 1906, 142, 885; Pfeiffer, Ber. 1904, 37, 4620; Rosenheim and Levy, Zeitsch. anorg. Chem. 1905, 43, 34; Hibbert, Ber. 1905, 39, 160; Lemoult, Compt. rend. 1905, 141, 1241; Berthaud, *ibid.* 1906, 143, 1116; Barber, Monatsh. 1906, 27, 379; Anschütz, Annalen, 1907, 358, 92; Michaelis and Linke, Ber. 1907, 40, 3419; Autenrieth and Geyer, *ibid.* 1908, 41, 146; Steinkopf, *ibid.* 3571; Pistschimuka, *ibid.* 385, 4; Levi Malvano, Atti R. Accad. Lincei, 1908, [v.] 17, i. 847: Swartz, Bull. Acad. Roy. Belg. 1909, 60; Luff and Kipping, Chem. Soc. Trans. 1909, 1993; Arbusoff, J. Russ. Phys. Chem. Soc. 1910, 42, 395).

For detection and estimation of phosphoric acid *v.* Analysis.

PHOTOGRAPHY. *Introductory.* — Photography is the art by means of which pictorial records are obtained by the action of light on certain substances. Although many bodies undergo permanent or temporary changes when exposed to light, not all of these are suitable for the object indicated; indeed, the number that may in practice be utilised is limited. In the practical production of these records the compounds of silver, iron, and chromium are alone of real value.

The making of a photograph is in the ordinary way divisible into two branches, the making of the negative and themaking of the positive, which may take the form of a picture to be viewed by reflected or transmitted light—a 'print' or a 'transparency,' to specify the terms usually adopted. In view of the fact that the time factor is important in negative processes, the most sensitive bodies are employed for this purpose, *and in the present state of knowledge* silver compounds, actually the halides, are alone suitable, whilst for the positive methods, silver, iron, or chromium are indifferently employed. Whatever operation is in question, and whatever compound is employed, two conditions are essential—the substance must possess sufficient sensitiveness and its physical and mechanical conditions must conform to the requirements of picture-making.

The photographic negative is obtained by projecting an image by means of a lens on to the sensitive surface, and the effect of the action of light once initiated is converted into a visible and permanent image by subsequent methods.

The negative so formed is employed to regulate the action of light on the surface employed for making the positive. This regulation may be effected by exposing the surface to light in contact with the negative or an image of any determined size may be projected by optical means on to the surface. In no case is the action complete by exposure alone, but requires subsequent chemical treatment to complete this action and to inhibit further change. Disregarding observations which showed that certain bodies became changed under the influence of light, the birth of photography in the sense specified and generally understood may be said to date from the experiments of Wedgwood, described by Davy in the Journal of the Royal Institution in 1802. Wedgwood had found that when paper impregnated with silver nitrate was exposed to light it darkened, this darkening being due to the reduction of the silver salt, and in this change the organic sizing in the paper played the predominant part.

The experiments of Wedgwood were carried a step further by Davy, who showed that silver chloride was more sensitive to light than silver nitrate, and that white leather as a support gave pictures with less exposure to light than was possible with paper. Here, again, is evidence of the enhancement of sensitiveness due to the halide being in contact with organic matter capable, as we now know, of acting as a halogen absorbent. Images produced by the aid of the solar microscope were readily obtained, but there was lacking the means of rendering these images permanent in daylight. Rather out of the path of the direct line of experiments, which in the early days centred around the silver salt, was the observation of Wollaston, in 1803, that gum guiacum was sensitive to light, but this departure in investigation gave what eventually proved to be a more useful addition to knowledge, when it was shown by J. Nicephore de Niépce, in 1814, that a thin film of bitumen became, after prolonged exposure to daylight, insoluble in its most usual solvents. In 1827, Niépce was refused the permission of the Royal Society to communicate his results on the ground that the process was a secret one. A few years later, in 1824, Daguerre commenced his experimental work, destined to become fruitful, and in 1829 Daguerre and Niépce worked as partners. The image produced by Niépce was a negative image on silver plate, and the shadows were therefore represented by the silver plate, and it was necessary that the uncovered parts should be darkened and the parts covered by the bitumen should be light. Daguerre applied iodine vapour to the plate and afterwards removed the bitumen image, noticing in the course of his experiments that the silver iodide changed on exposure to light. Daguerre conceived the idea that a surface of silver iodide might be used to produce an image, but it was only by an accident that he discovered the process of development (viz., exposure to the vapour of mercury) so to render it visible, although the mode by which the development was traced to its cause was an excellent illustration of the deductive method applied to the discovery of a scientific truth. The result of these experiments was that in 1839 the discovery of the daguerreotype was given to the world. The process of Daguerre became of considerable importance, and may be said to be the practical starting point of picture-making by photography. As worked eventually, the method consisted in exposing a plate of silvered copper to the vapour of iodine, then bromine, and finally iodine, which plate was then exposed in the camera. After exposure, the 'latent' image formed by light was developed by submission to the vapour of mercury, and the picture was then fixed by the action of sodium thiosulphate, the final image consisting of an amalgam of silver although it was sometimes 'toned' by means of a solution of gold.

In the same year, Fox Talbot gave the results of some experiments in what proved to be the starting point of a fruitful series of investigations, when he demonstrated before the Royal Society (first mentioned by Faraday before the Royal Institution the same year) the possibility of producing negative and positive images on silver chloride. Paper impregnated with common salt was steeped in a solution of silver nitrate and eventually dried. This paper contained silver chloride in the presence of an *excess* of silver nitrate—an important detail. Images were produced by exposing the paper under opaque and semi-opaque bodies, such as ferns or lace, and a facsimile in black and white was produced, these images being fixed by the application of solutions of bromides and chlorides. From the negative impression, positives were then obtained. Valuable improvements were made by Reade (one of the early experimentalists) who had previously used tannin as an accelerator to increase the sensitiveness of silver chloride when making pictures, after the fashion of Davy with the solar microscope, and had taken advantage of Herschell's discovery of the solvent property of sodium thiosulphate for halide silver salts, to use this body as a fixing agent for the images. Reade suggested the employment of gallic acid in the presence of silver nitrate as an accelerator for Fox Talbot's surface, and the further use of the same agents to develop the image produced on exposure.

Daguerre's discovery of the photo sensitiveness of silver iodide was now utilised by Fox Talbot who, in 1841, patented the 'Calotype' process. In this method paper, impregnated with silver iodide, was exposed to an image in the camera in the presence of silver nitrate, acetic and gallic acids, and the slightly visible image produced was then developed by the application of a more concentrated solution of the gallo-nitrate, this image being eventually fixed by sodium thiosulphate. There resulted a negative record. In 1844, Fox Talbot issued a book entitled The Pencil of Nature, which was illustrated by positive pictures on silver paper from Calotype negatives.

The advantages of glass as a support in lieu of paper were advocated by Herschell in 1843, who then showed a picture produced on silver chloride deposited on that substance, but the want of a suitable vehicle was a deterrent. This drawback was partly removed by Niépce de St. Victor, who showed in June, 1848, that albumen could be used for the purpose, and produced negatives by the method. A great advance was made by Scott Archer the same

year, who taking advantage of Maynard's 'collodion' (a solution of nitrated cellulose in ether-alcohol made first in 1847 from Schönbein's 'gun cotton' prepared for the first time the previous year), experimented with this preparation as a vehicle for holding the silver halides on glass, and actually in the autumn of that year produced the first negative by what became eventually to be the famous 'wet collodion' process. It was not, however, until 1851, that the method was published by Scott Archer as a really practical system. From 1851 to 1871 the collodion process in one form and another maintained empery, and there are abundant signs that no other method was anticipated by the large and increasing number of photographers, although the fact that Sayce and Bolton had, in 1864, produced an *emulsion* in collodion, and Smith had patented an emulsion of the halides in gelatine the following year, might have given an impetus to seek for new methods to overcome the difficulties incident to the use of collodion which it is permissible to think would never have enabled photography to have become the important branch of industry that it is to-day.

Writing to the British Journal of Photography on September 8, 1871, Dr. R. L. Maddox, a Southampton physician, gave the result of 'somewhat careless experiments tried at first on an exceedingly dull afternoon.' Dr. Maddox found that it was possible to emulsify silver bromide in gelatine by mixing with a solution of the colloid, cadmium bromide, and then adding silver nitrate. The emulsion so prepared was spread upon glass and dried, and the surface then exposed to light under a negative. The plate showed no image, but on wetting and treating it with a solution of pyrogallol in water, a faint picture appeared. Subsequent plates were then treated in a similar manner, and the faint image was afterwards strengthened by treatment with a solution of pyrogallol to which silver nitrate had been added. Maddox subsequently applied the emulsion to paper, thus anticipating the modern gelatino-bromide paper destined not to be commercially produced until 1874.

Many experimentalists worked at the silver bromide emulsion process, and in 1874 Kennett placed upon the market the first commercial dry plate, and thus was commenced what has become a large and world-wide chemical industry, viz. the manufacture of the gelatine dry plate.

One year before the publication of Fox Talbot's process, Mongo Ponton showed that a mixture of a soluble bichromate with organic colloidal matter became changed on exposure to light. This observation and its extensions remained unnoticed for some years, but the application was seen subsequently in the photogravure process of Fox Talbot, the collotype method of Poitevin, the Woodburytype of Walter Woodbury, the photo lithograph of Osborne, all important photo-mechanical processes (*see* Photo-Mechanical Processes), and in pure photography it led, by the labours of Poitevin, Pouncey, Salmon and Garnier to the carbon process, first rendered commercially successful by Swan, by Sawyer, and by Johnson (*see* Chromium Printing, p. 245).

For many years methods for producing positives were almost wholly those depending upon the changes which took place in silver and chromium salts, the medium being either collodion or gelatine, but in 1873, Willis, who had been investigating the photo-sensitiveness of ferric salts—first practically utilised by Herschel in 1842, in the invention of the 'ferro prussiate' or 'blue print' method—introduced the platinotype process destined to become one of the most important and beautiful processes in photography. In this method, paper coated with ferric oxalate, a salt of platinum and of silver was exposed under a negative, and the image so produced was developed by floating the paper upon a hot solution of an alkaline oxalate. This process passed through several modifications and eventually its use became firmly established.

When the gelatine dry plate came into use it was quickly found that photographic negatives could, by its aid, be made with a much shorter period of camera exposure; in other words, the silver halide, by its particular condition (chemical and physical), could be made much more sensitive to light than was the case of the silver halide in collodion. Although collodion plates could be made of different degrees of sensitiveness, the range and the maximum was always less than in the case with gelatine. But there was another factor of importance, often overlooked, which is that the different mode of development as compared with that of collodion plates contributed largely to the increase in speed. The sensitiveness, or, to speak from a practical point of view, the 'speed,' which is not the same thing, of the modern dry plate is something which has only been attained by long and careful experiment under the conditions of manufacture on a working scale, for there is something about the dry plate which seems to defy mere laboratory elucidation alone, using the term to denote manufacture on a small scale. Not only has there been this gain in speed, but other things equally important as range and gradation rendering properties, which together with speed have been the open sesame to many fields closed to the collodion process. But there remained with the gelatine plate, as with the collodion plate, one very important limitation. The curve of its spectral sensitiveness was entirely different to the luminosity curve of the human eye, and this led to the well-known falsity in the rendering of the relative brightness of coloured objects and, because of this, to something which is often forgotten, viz. false gradation in tone. To overcome this defect Vogel, influenced by some observations made when using Stuart-Wortley's uranium emulsion worked out the previous year, had, in 1873, recommended the addition to collodion of relatively minute quantities of a colour stuff, *corallin* (a dye stuff of the rosolic acid series), which conferred upon the substance so treated a decided sensitiveness for the yellow-green, and this innovation was the commencement of orthochromatic photography.

In 1875 Waterhouse suggested the use of *eosine* for the same purpose. Ives proposed and used with success *chlorophyll*, which conferred orange sensitiveness, alone in 1879, or in conjunction with *eosine* in 1885. In 1882 eosine was applied to dry plates by Taillfer,

and in 1884 erythrosin was used by Eder. The first English orthochromatic plates made commercially were issued in November, 1886. In 1903 Miethe introduced ethyl red (diethyl-iodocyanin iodide) for the purpose, and in 1904 König gave to photography a valuable set of *iso*cyanin colour stuffs under the names of *pina-chrome*, *orthochrome*, and *pinacyanol*, the use of which greatly removed the reproach of deficient colour sensitiveness from the dry plate. Still further developments were made by Pope from 1917 onwards, by the *iso*cyanin compounds issued under the names of Sensitol red, green, and violet.

No outline of the history of photography, however brief, would be complete without allusion to the influence brought about by the use of different development agents. The ' speed ' of the modern dry plate is far in advance of the earlier sensitive surfaces used for negative making, but in this speed, as previously stated, the part played by the mode of development is considerable. When the collodion dry plate was developed by means of an alkaline reducing agent (ammonia-pyrogallol) it was found that the exposure could be considerably reduced compared with that necessary when the plate was treated with an acid reducing agent in the presence of free silver nitrate after the manner of the wet collodion plate. It was found, however, that when attempts were made to still further reduce the exposure by increasing the concentration of the developer that the plates ' fogged,' that is, the unexposed portions of the plate were also affected by the developer. With the gelatine dry plates, however, much more powerful developers could be employed, owing to the restraining influence of the gelatine with the consequent reduction in the exposure necessary to produce a satisfactory negative. The early dry plates were developed with ammonia-pyrogallol (introduced by Russell in 1862), and later the ammonia was replaced by sodium or potassium carbonate or the caustic alkalies or with ferrous oxalate (Carey Lea, 1877), the latter agent being more used by continental photographers than by those in Great Britain; indeed, its use persisted with them to a consider-able extent long after its employment had been almost abandoned in England. The alkaline developer as against the ferrous oxalate permits of a considerable reduction in exposure. Quinol with an alkali was introduced as a dry plate developer by Abney in 1880, but this agent, not being so satisfactory as pyrogallol, never had the vogue of the latter agent. In the same year Eder and Toth demonstrated the develop-ing properties of an alkaline solution of catechol. Many agents were subsequently brought into use, as, for example, *p*-aminophenol with caustic alkali in 1888 by Andreson, and the following year *eikonogen*, the sodium salt of α-amino-β-napthosulphonic acid, described by Meldola (1881), was brought out as a devcloping agent by Hauff, and also later by Andrcson. There followed a number of othcr agents, the chief of which were *amidol* (diaminophenol hydrochloride), *glycin* (*p*-oxyphenyl glycin), and *metol* (methyl *p*-amino-*m*-cresol) by Hauff in 1891. Many of the substances had only a brief use, and to-day, by a process of the survival of the fittest, the chief agents in usc are pyrogallol, metol, alone or in combination with pyrogallol or quinol, paraminophenol, and amidol. In every developer there is employed as preservative and stain preventer the agent sodium sulphite, first introduced by Berkeley in 1882 as a preservative for pyrogallol. The alkalis generally employed are sodium carbonate and caustic potash or caustic soda, ammonia as an alkali in the developer being practically obsolete.

Lumière and Seyewetz have shown that in order that a benzene derivative may act as a developer there must be at least two groups substitutcd in the same nucleus, either two hydroxyls or two amino groups, and that these must be in the *o*- or the *p*- position, no *m*-derivation functioning as a developer. If more than two groups be introduced then such a substance becomes more energetic, and that if the extra group be an amino group the body can act as a developer without the aid of an alkali. Such a substance is amidol (dia-minophenol hydrochloride), which is employed with sodium sulphite alone.

In practical negative and print making the sensitive agent must be held in same medium, which in turn requires a support, although, as in the case of early experiments where paper was employed or in the silvered plate of Daguerre, the medium and the support are one and the same. The media used to attain the end have been albumen, collodion, and gelatine, and in each case these bodies have played a very important part, both chemically and physically. The support came soon to be the most obvious one, viz. glass, which in many respects is ideal. The drawback to glass is, however, its weight and brittleness, and, more-over, it does not lend itself to the obvious employment of a *roll* of sensitive material as against one which is always kept flat. As early as 1854 a device for holding sensitive paper in rolls was patented by Spencer and Melhuish, and in the following year devices for the same purpose were introduced by Barr and Relandin. In 1856 Parkes proposed and patented the use of a transparent support of celluloid, which was commercially manufactured by Hyatt, U.S.A. Six years later than this date Warnerke pro-duced a ' stripping film ' to be used in roll form, and in 1884 John Carbutt, U.S.A., produced a gelatine emulsion-coated celluloid. A great advance and one that gave, by its practical character, great impctus to the use of roll-able sensitive material was the negative paper of Eastman, which was improved by coating the emulsion on soluble gelatine substratum, which permitted the removal of the negative film after completion to a flexible gelatine skin or to a rigid support of glass. Of far-reaching effect has been the Eastman introduction in 1889 of rollable celluloid coated with gelatino bromide emulsion, an important addition being made two years later by the provision of the system by means of which this film could be loaded into the camera in daylight. The effect brought about by these introductions has been enormous, and to-day the almost universal use of photography as a pastime, with its collateral developments, is due almost entirely to the employment of the rollable celluloid film. The fact that a suitable flexible material as a support

for the sensitive surface became available has had another far-reaching effect, in that it has permitted the development of Marey and Muybridge's (1870–72) original motion pictures, and this development has resulted in modern Kinematography.

From an early date observation had shown that the changes which occurred when silver salts were exposed to light (and not alone silver salts) were not solely simple darkening effects, but when the substance was exposed to the influence of coloured light the altered body bore some relation, with respect to hue, to the exciting cause. In 1801 Ritter showed that the different spectral 'rays' produced different effects, and later, Seebeck (1810) observed certain relations between the two. Many investigators have confirmed these experiences, notably, Wollaston, Niépce, Becquerel, Zenker, Carey-Lea, Wiener, du Hauron, and Lippmann. In 1861 Clerk Maxwell, in a lecture on the theory of vision, considering Young's hypothesis on the primary colour sensations, assumed that there exists in the retina three sets of receiving nerves which can be excited in a particular manner—by light corresponding to certain spectral regions—producing the sensations we term *red*, *green*, *blue-violet*, and that all the sensations that we explain as 'colours' may be produced by the stimulation of these sets of nerves to appropriate degrees. In demonstration of these principles photographs were made of a series of coloured ribbons through colour screens which were red, green, and blue, and afterwards positives from these negatives illuminated by light of the hues of the screens were projected and the colour images produced were superimposed. Clerk Maxwell in this way produced a photographic representation in colour of the original object, marred only by reason of the deficiency in the colour sensitiveness of the photographic material then available. In 1869 there was published from the pen of Louis Ducos du Hauron, La Photographie des Couleurs, where was outlined, in anticipation, most of the methods since employed which this author considered could be utilised for producing photographs in natural colours, including the most practically satisfactory of the present-day methods, the so-called 'screen plate' processes. Largely by the work of Ives the original method of Clerk Maxwell has been developed and furnishes, so far as beauty and accuracy are concerned, the most perfect results so far obtained by any colour process, whilst to the work of the brothers Lumière (Autochrome), communicated to the Académie des Sciences, May 30, 1904, and the process of Finlay developed finally by this worker in the Paget Company, we owe the best examples of the 'screen plate' processes based upon the original suggestion of du Hauron, both of which methods have yielded results of a striking character.

As a simplification, instead of the use of three colours, two have been employed with a fair measure of success. By this plan negatives are made through an 'orange-red' and a 'blue-green' screen of particular hues, and the positives illuminated by suitable 'orange-red' and 'blue-green' are projected and superimposed, the 'taking' screen and 'projecting' screens differing, however, in hue, actually in the extension of the respective spectral bands. Such a process employed in kinematography was known as 'Kinemacolour,' which some years ago deservedly attracted considerable attention. An application of the two-colour principle is shown in the process 'Kodachrome' (J. G. Capstaff, Eastman Kodak Laboratories), by means of which colour prints are obtained, and by this plan pleasing results are possible with certain types of subject. For kinematography the two-colour principle working subtractively has been developed by Capstaff, who produces red and green pictures on opposite sides of a double-coated celluloid film which are projected in the ordinary manner when a two-colour subtractive picture is produced upon the screen. The three-colour additive process has been utilised for kinematography, the best of the applications being that of Gaumont.

A valuable contribution to the early history of photography is given by Waterhouse (*see* History of the development of Photography with the salts of silver, Photo. Journal, 1903, xliii. 159–178); *see* also Litchfield (Alleged discovery of Photography in 1727, *ibid.* 1899, xxiii. 53–58); also Eder (Geschichte der Photochemie und Photographie, Halle, 1891); and Schiendl (Geschichte der Photographie, Wien, 1891).

Processes.

In the practice of picture making by photography the operations may be arranged in two distinct groups, although the basic principle involved is the same in both cases. The first operation consists in making the negative and the second the positive or print. It is convenient to consider the two groups of processes involved separately, commencing with those relating to the making of negatives. A negative once obtained may be used for print making by any of the processes, but for the best prints the negatives should possess a certain range of gradation, according to the particular sensitive surface that is used.

Negative-making methods.—There are three negative-making processes in use, viz. the 'wet collodion,' 'collodion emulsion,' and the 'gelatino-bromide,' these taking their names from the respective medium employed, viz. collodion and gelatine. It is often assumed that the collodion processes are little used, having been replaced by the modern gelatine dry-plate method, but such an assumption is erroneous, for collodion negative processes are to-day very largely used in the extensive industry of photo-mechanical photography, for which purpose wet collodion is particularly suitable, both on the grounds of technique and economy. Collodion emulsion is suitable for the copying of pictures in colour, inasmuch as it readily lends itself to the application of sensitisers, although it is now largely replaced by the modern panchromatic dry plate. But although important in this respect, collodion is little used for ordinary negative making in pure photography (except copying), which depends entirely upon the gelatino-bromide process.

There are three collodion methods: the 'wet collodion' process, where the silver halides are exposed in the presence of free silver nitrate; the 'dry collodion' process, in which the free silver nitrate has been washed away after

sensitising and the film treated with a solution of an organic substance, capable at once of absorbing halogens and acting as a protective coating or varnish against the undue influence of air and moisture, as, for example, albumen; and the 'collodion emulsion' process (Sayce and Bolton, 1864), in which the silver halides are formed as an emulsion in the collodion before application to the glass plate. The convenience of the two latter processes was, for work away from the photographer's studio, considerable, for the plates could be carried in the dark slides ready for use, whilst with wet collodion it was necessary to take the whole of the requirements for plate preparation and finishing into the field. This resume only gives a brief notice of the collodion bath processes, of which there was a considerable number of modifications.

'*Wet*' *collodion. General.*—A solution of pyroxylene (principally di-nitro cellulose) is prepared in a mixture of equal parts of ethyl ether and ethyl alcohol. This constitutes plain collodion. The collodion is then 'iodised' by the addition of an iodide and a bromide, generally those of ammonium or of cadmium or a mixture of both, and to the solution is added a trace of free iodine. A piece of glass is then coated with the iodised collodion, and when the film is 'set,' owing to the partial evaporation of the solvents, the plate is immersed in a solution of silver nitrate slightly acidified with nitric acid, this solution being technically termed 'the bath.' When the formation of the silver halides is complete the plate is withdrawn from the 'bath,' is drained, and then exposed to an image in the camera. After exposure the plate is treated with a solution of ferrous sulphate acidified with acetic acid, when the image is 'developed.' The film is then subjected to the action of a dilute solution of potassium cyanide (or sodium thiosulphate), when a soluble double salt is formed, which is eventually removed by the application of water. The initial opacity of the image being seldom sufficient, it is then treated with a further quantity of the developer, to which has been added silver nitrate, or in place of the ferrous sulphate a solution of pyrogallol acidified with citric acid may be used. This process is a continuation of the development, and is sometimes called 'redevelopment,' to distinguish it from other processes of increasing the opacity termed 'intensification' (*q.v.* p. 240). Generally the 'redevelopment' method is used where only slight increase of opacity is necessary, and where it is required to preserve the gradation. More often, and generally for that type of negative for which wet collodion is now used, the application of the so-called 'density' intensifiers is necessary, a typical process being to treat the image to a solution of cupric bromide when it is bleached, and there is formed a bromide of silver and cuprous bromide complex. After slight washing the complex image is treated with a strong solution of silver nitrate, when an opaque black image results. It will be observed that the silver halides are exposed in the camera in the presence of moisture and free silver nitrate. If the silver nitrate be removed by washing then the sensitiveness of the halides is considerably reduced, but may be restored to a considerable extent by flowing over the plate a fresh solution of silver nitrate. The silver nitrate is said to act as a 'sensitiser.' Certain other substances, which must be halogen absorbents, function in the same manner, but none so efficiently as the metallic salt. The precise nature of the change which takes place is not known. It is sometimes assumed that a sub-halide of silver is formed. This is merely a convenient hypotheses which is, however, lacking in proof. All that can be said with certainty is that whatever may be the change brought about by the action of light the silver halide which has been acted upon behaves during development in a different manner to that which has not been affected. When to the system silver halide, silver nitrate, and water, there is added ferrous sulphate, this ferrous sulphate reduces the silver nitrate and metallic silver is precipitated, the acetic acid acting merely as a restrainer. The minute particles of metallic silver formed by the action of the reducer are attracted to these portions of the silver halide which have been light affected and in proportion to the light action, so that the greatest amount of silver goes to those parts most affected by light.. This forms the initial image which can be shown to be practically invisible. But by crystalline attraction every minute particle of freshly formed metallic silver attracts other particles, and the image soon becomes visible and grows in intensity so long as there is any free silver nitrate left to be reduced by the developer. The increase of density which follows from the fresh application of reducer and silver nitrate will be readily understood, it being merely a continuation of the initial development process. It will be observed that the silver halides themselves contribute no material to the image, being immune to this form of developer, and are removed by the action of the potassium cyanide followed by water or by the sodium thiosulphate when used in lieu.

Many agents contribute to sensitiveness and to opacity of the image. The pyroxylene, the particular soluble halides used in iodising, the amount of free iodine in the collodion—which liberates on sensitising free nitric acid in the film, which is probably adsorbed to the silver halides—the concentration and acidity of the silver nitrate 'bath,' the temperature of working, and the reducing agent used as a developer. Thus, for example, considerably more exposure in the camera is necessary if a solution of pyrogallol with citric acid be used in place of the usual ferrous sulphate solution, although the *photographic opacity* is less in the case of the former agent with pyrogallol, as the coloured oxidation product unites with the metallic image. The particular sample of pyroxylene exercises an influence on the opacity of the image, being greater when a gelatinised cotton is used for making the pyroxylene in place of a cotton free from soluble organic matter. The maximum opacity appears to be yielded by a collodion iodised with cadmium iodide alone, which has been kept for a considerable time, a solution of acidified pyrogallol being used for development.

'*Dry*' *collodion.*—A collodion 'wet plate' may be converted to a 'dry plate' by washing the plate after sensitising to remove the free silver nitrate and afterwards applying a

solution of certain organic substances, which will play the part of halogen absorbents on exposure of the plate, and then drying. The plates after the exposure are developed as wet plates by the application of an acid developer to which free silver nitrate is added at the moment of application, or with an alkaline developer in the absence of free silver nitrate. These plates were known as 'dry plates with the bath.' The collodion plate after sensitising is carefully washed free from silver nitrate and is then drained and then treated with the preservative and dried. After exposure the plate is washed in water and developed with an acid solution of ferrous sulphate to which is added silver nitrate, or the plate may be developed with an ammoniacal solution of pyrogallol and followed (by the addition to the solution) with citric acid, acetic acid, and silver nitrate. This mode of development presents features of considerable interest. The combined halide film is only partially affected by the ammoniacal pyrogallol, the silver iodides being unaffected. When a faint initial image is produced the alkali is neutralised by the acid added, and the attractive influences of the affected iodide comes into play. The silver reduced by the now acid pyrogallol is precipitated on the iodide, and also upon the silver image formed by the reduction of the silver bromide. The plate is then 'fixed' in the usual manner, when the image may be then intensified if necessary. Very many processes for the production of dry plates with the bath were employed. Those who may desire as a matter of interest to pursue the subject further should consult the 6th edit. of Hardwich's Photographic Chemistry (London 1861). The exposure required for these dry plates varied with the form of the development, being least with the alkaline developer. The plates described, although allowing great 'latitude' in exposure, were generally less sensitive than the 'wet' collodion surfaces.

'*Collodion emulsion.*'—If in a plain collodion there be dissolved an ethyl alcohol soluble halide, as cadium or zinc bromide, and to the bromised collodion there be added an alcoholic solution of silver nitrate, the silver halide, provided the addition has been correctly made, will be formed in a fine state of division and highly sensitive to light. The silver nitrate or the soluble bromide may be in excess. The emulsion now contains the soluble reaction product—the cadmium nitrate or zinc nitrate, as the case may be. This must be removed either by washing the plate after coating or by precipitating the emulsion by means of water, then washing with further water, and afterwards redissolving the 'pellicle,' after removal of the washing water, in fresh ether-alcohol. The former yields an 'unwashed' and the latter a 'washed' emulsion. The advantage of a washed emulsion over an unwashed emulsion is that it will keep. An unwashed emulsion after a time rapidly loses sensitiveness, especially if prepared with an excess of soluble silver salt. When an unwashed emulsion is employed it is practically necessary to use a preservative, and the same may be said when a washed emulsion is used if the plate is to be dried before use, otherwise the negatives will probably show spots that refuse to develop when the plates are kept. (This trouble does not appear when the 'unwashed' emulsion films are used before drying.) Since to-day collodion emulsion films are only used in the studio the plates are coated as required, there being no necessity for drying.

The exposed emulsion film may be developed with an alkaline pyrogallol or a ferrous oxalate or ferrous citro-oxalate developer. Modern collodion emulsions are, however, almost invariably developed with quinol and potassium carbonate. After development fixation is effected by sodium thiosulphate, as the image is liable to be attacked by the use of potassium cyanide.[1] Intensification may be effected after fixation by any of the usual methods.

The processes involved in the development of an emulsion film by the alkaline developer differs from that which obtains with a wet collodion plate where a soluble silver salt is present. The silver bromide affected by light is reduced by the developing solution, and the product, which may be taken to be almost wholly metallic silver, save for a little organic matter, forms the image, whereas in the wet collodion plate the image is formed by the silver produced from the reduction of the free silver nitrate by the acid developer employed, this silver being deposited on the silver halide affected by light. By the addition of a very small quantity of a colour sensitiser (*q.v.*) in the form of an alcoholic solution the spectral sensitiveness of the emulsion may be considerably extended. One of the first of these emulsions was described by Jonas in 1891 (British Journal of Photography, March 18, 1892), who used an alcoholic ammoniacal solution of silver eoside or silver erythroside in conjunction with ammonium picrate, the effect of which latter agent was to 'damp' the excessive sensitiveness to the more refrangible end of the spectrum. This was probably the first use of the 'non-screen' principle, by means of which the use of the so-called 'yellow screen'—the purpose of which is to absorb the ultra-violet and to partially absorb the blue—on the lens was avoided. This principle is now adopted in the manufacture of certain orthochromatic dry plates. The emulsion of Jonas gave remarkably fine results. Since the introduction of the modern *iso*cyanin colour stuffs their employment has been common, either by the addition of an alcoholic solution of the particular compound to the bulk of the collodion emulsion, or by treating the coated plate with an aqueous solution of the 'sensitiser.'

It is not proposed to give any further details respecting dry-plate processes with the bath or collodion emulsion, since the former is obsolete and the latter is a commercial product readily obtainable. The wet collodion process is an important method in daily use.

In view of the undoubted convenience of the gelatine dry-plate process, where the sensitive plates are sold ready for use, it may be convenient to state briefly the advantages of the wet collodion method. Economically the process is cheaper, more particularly for plates of large size, and in practice in the studio negatives are made more rapidly than by any dry-plate method. The fact that some gelatine plates are of far greater 'rapidity' than wet plates must

[1] The attack is mainly due to the presence of cyanate.

not be allowed to obscure the fact that for certain classes of subject 'broken tone' (*see* Photo-Mechanical Processes), as line and screen 'half-tone negatives,' dry plates of relatively low rapidity are necessary to yield the type of negative required. Of the whole time occupied in the making of a negative the time taken for the exposure of the plate in the camera is only a small proportion, the after operations—development, fixation, intensification, washing and drying—are much quicker with wet collodion plates than with gelatine dry plates, although certain kinds of dry plates (thin-film dry plates) can be dealt with very quickly.

Wet collodion negatives properly prepared are characterised by great cleanness and freedom from fog, even when high density is obtained, a condition not easy to attain with many subjects when using dry plates, and this enables printing to be accomplished easily. The material composing the image in a wet plate is on the surface, whilst in a gelatine dry plate it is diffused through a film of appreciable thickness, a condition inimical to sharpness, although the thin-film process dry plates approximate to this condition.

For these reasons the use of the wet collodion for certain purposes is likely to persist, more especially in view of its undoubted economic advantages. The principal drawback to the use of wet collodion is its limited spectral sensitiveness, but for subjects in colour the panchromatic dry plate is employed.

For practical details of the collodion processes, *see* Instruction in Photography (Abney), and Collodion Emulsion (Klein).

The gelatine emulsion process.—If to a 'solution' of gelatine in water which contains an alkali bromide there be added slowly and with careful agitation a solution of silver nitrate insufficient to decompose the alkali bromide, both solutions being at a temperature of about 40°C., there will be produced in the early stages of the addition a faintly turbid mixture which eventually becomes distinctly milk-like in character, this appearance being due to the formation of silver bromide. If the mixing has been properly conducted the halide particles will be small in size but of varying sensible magnitude, and some will be colloidal. The particles under the circumstances will be sufficiently fine to pass through a filter paper of close texture, but the mixture on standing at the temperature stated will deposit some portion of the halide, that portion which may be regarded as the suspension. To the mixture produced by the method stated the term gelatino-bromide of silver emulsion is applied. If, after the mixing operation, a thin film of this emulsion, spread upon glass by pouring, be examined by the transmitted light from a metallic filament glow lamp the colour of the film will appear of orange or orange-red hue, which is a physical demonstration of the small size of the halide particles. If the emulsion be allowed to 'set' to form a gel and then be broken up to form shreds, these shreds can be freed from the soluble content—excess of soluble bromide and the alkali nitrate formed in the decomposition—by washing with cold water, and on draining carefully the shreds from the adhering excess of water and remelting a liquid emulsion will again result. If glass be then coated by means of a thin uniform film, and this film be allowed to set and then dried in a current of air, a gelatine dry plate results. Such a plate will possess few properties of value, but it serves to demonstrate the bare principle. It will be extremely insensitive or, in the usual parlance, of very low 'speed,' [1] it will be unable to render to any appreciable extent gradations of light and shade, but it may yield on suitable development, if it has received a sufficient exposure to light, an image, the characteristic of which will be excessive contrast of light and shade as compared with the relative brightnesses of the luminous image to which the plate was exposed.

A reference has been made in the historical introduction to the original experiment of Maddox, in 1871. The emulsion of Maddox was prepared with the silver nitrate largely in excess. In the conditions given in this note the silver nitrate is always in deficiency with respect to the alkali halide, for were the reverse to be permitted the silver nitrate, at the temperature stated, would be readily decomposed, with the result that the emulsion would show 'fog' [2] on subsequent treatment in negative making, and to avoid this defect, and for other reasons, the alkali halide is now invariably maintained in excess. Maddox stated that on keeping some of the emulsion for three days its sensibility had greatly diminished. Johnson, towards the end of 1873, proposed the preparation of an emulsion with an excess of soluble bromide, and this procedure was destined to be the practice in the future. When such an emulsion was kept in a 'gel' form at ordinary temperature for several days plates when coated showed an

[1] The term 'speed' and 'sensitiveness' are frequently used indiscriminately as if they were identical, but this is not strictly correct, the term 'speed' connoting more than the word 'sensitiveness.' In the technique of negative making, as it is practised, the term 'speed' would appear the better of the two for the qualities to be conveyed by either word, *see* F. W. T. Krohn, Photo. Journal, 1918, lviii. 179.

[2] 'Fog' is the technical term applied to the veil over the image due to the presence of metallic silver (whether colloidal or in particles of sensible magnitude) which results from the development of silver halide grains which contain 'nuclei' or centres of affection. The nuclei may arise from the presence during the process of manufacture of substances in the emulsion which have the property of making the grain developable, or by the influence on the emulsion film of light and other forms of energy.

The common appearance of fog is that of a grey veil over the image which shows, naturally, the more pronounced over the less opaque parts of the negative, and should not be confused with 'stain,' for although the appearances are in some cases similar the causes of the particular appearances may be different.

Apart from the inherent tendency of the emulsion to produce 'fog' (emulsion 'fog'), it may arise from unsuitable development either in the composition of the particular developer or the precise conditions under which the operation is conducted. To this second form of 'fog' the term 'chemical fog' is applied. When the fog is due to the emulsion the extent to which it is produced is to some extent a function of the particular developer and the conditions. When the fog is chemical 'it may show differences from the image in structure and in grain distribution' (Nietz). Most emulsion films, especially the more sensitive, tend to show fog on development, though with clean working emulsions and suitable development the amount is negligible. Any emulsion film with unsuitable development will show 'chemical fog.'

With films of standard production it may be taken that in the total 'fog' produced, emulsion 'fog' plays a relatively small part. The two forms when occurring in a negative cannot be separated.

increased sensitiveness over those prepared from the emulsion before keeping.

Bennett in 1878 further proposed the digestion of the emulsion at 32°C. for 6–7 days, when there was found to be a great gain in sensitiveness, and this discovery marked an epoch in emulsion making. Wortley later digested an emulsion at 65°C., and in 1879 Mansfield advocated that the emulsion should be brought to the boiling-point and maintained for a short time in this stage, a process, however, which rapidly destroyed the setting power of the gelatine. The method of avoiding the difficulty that ensued from the destruction of the gelatine was demonstrated by Bolton, who was the first to suggest (1873) the procedure which eventually became the method in general use, and still remains so. Bolton emulsified the silver halide in the presence of a small amount of gelatine, and after digestion added sufficient fresh gelatine to give the necessary firmness to the jelly formed on cooling the emulsion. If an emulsion be freed from an excess of alkali halide and be then digested it will be found that the plates prepared show no gain in sensitiveness over those made from the emulsion before digestion. The presence of an excess of the soluble halide is necessary for the production of that molecular modification of the silver bromide which possesses enhanced sensitiveness. The excess alkali halide fulfils several functions. It ensures the conversion of the whole of the silver nitrate so that no 'fog' is produced, owing to the action between the latter salt and the gelatine, it prevents the decomposition of the emulsion, to which there is a tendency in prolonged digestion, and it produces the sensitive modification of the silver halide, the so-called 'ripening' of the emulsion. On digestion, in the presence of an excess of the alkali halide, the silver halide passes through a series of changes, involving an alteration of form and an increase of size, the salt being converted from the amorphous to the crystalline condition, and for this change it is necessary that there be present a solvent of the silver bromide, which part is fulfilled by the alkali halide. The first observer to draw attention to this phenomenon appears to have been Banks (Photo. Journal, xxii. 159) in the course of the discussion upon a paper by Hurter and Driffield on the latent image and its development. The amount of the excess is not unimportant, and many statements have been made by investigators as to the best value, but it is problematical whether the mode of establishing the optimum value then adopted would find favour to-day. It does not appear that any figures based upon the work of modern emulsion makers have been published. Eder and Abney, two of the most experienced of the early investigators, agree practically in giving the ratio 20KBr and 16AgNO3 and 20KBr and 15AgNO3 respectively. The changes which occur when an emulsion is digested are indicated to the eye by changes in hue. For a pure bromide emulsion the colour, which was originally yellowish-white by reflected light, takes on a greenish cast as the digestion proceeds, and the hue by transmitted light at each stage changes from the original orange-red to greenish-blue, but the colour changes given are only approximate, and they differ according to the mode of preparation of the emulsion. Incidentally with these changes in colour there is, as might be expected, a change in opacity, and the emulsion film of given thickness becomes less opaque. There is an optimium value with respect to the gain in sensitiveness by the digestion, for if the heating be allowed to continue unduly the silver halide becomes coarse and the plates 'fog' on development. Not only does the coarseness of grain act inimically with respect to the most desirable mechanical condition of the film, but it would be an error to assume that because an increase in grain size generally means enhanced speed, an increase in grain magnitude *necessarily* means increase in speed.[1] The possibility of producing a certain physical condition is determined by the conditions which obtain during the process of emulsification, thus, if it be desired to produce an emulsion for high-speed plates that fact must be borne in mind from the initial operation, for the digestion is only a stage in the progress. The principal determinants are the kind of gelatine employed and its concentration for the actual emulsification, the alkali halide and the silver nitrate content in the solutions to be mixed, the form, temperature, and the rate of emulsification, and the conditions of the digestion. The emulsion after digestion is cooled and the remaining gelatine is added. When the emulsion is cooled to setting the 'gel' is then washed to free the mass from the products of decomposition, is drained from excess of water, and is remelted and made up with distilled water to the required volume. Before this is done there is added a certain quantity of alcohol, an antiseptic, generally thymol or phenol, a small quantity of alkali halide and, in addition, chrome alum. The alcohol aids the flow of emulsion when coating the plates, and assists the permeability of the film to the developer, the alkali halide corrects any tendency to emulsion fog, and the chrome alum 'hardens' the gelatine and acts as a preventative to softening and expansion of the gelatine, which often causes the film to pucker or frill and to leave the support. Excess of alkali halide reduces the speed, and if plates exposed be kept for any length of time before development, especially in warm damp climates, will lead to a fading out of the latent photographic image (Baekeland). An undue amount of chrome alum will lead to a gradual hardening of the film and a reduction of its permeability to the developer. The use of the antiseptic is obvious.

The particular procedure adopted in emulsification and the subsequent treatment of the emulsion determines the dispersity of the halide salt. It has been demonstrated that the original idea that there was an alteration in the form of the original 'particle' or 'grain' of the silver halide during the 'ripening' process has a solid foundation of fact, and, further, that at a certain stage the grains of the halide assume a definite geometric form. The form of the 'grain' and the size are functions of the speed, but not necessarily its sole determinants. Bancroft (Report, Fifth International Congress of Photography, 1912, 118)—who assumes that the silver bromide grain is a complex of silver

[1] The increase in 'speed' due to digestion reaches the optimum value before the fogging point supervenes.

bromide, gelatine, and water—considers that there is no necessary connection between sensitiveness and coarseness of grain, and that it appears to be theoretically possible to make 'an almost infinitely fast plate having a very fine grain' (*see* also J. Phys. Chem. xiv. 650). This assumption appears to be borne out by examination of the successive productions in modern dry-plate manufacture, for the more rapid plates issued show a considerable reduction in grain coarseness over earlier examples. Fineness of grain has always been considered a factor of importance in the dry plate—and, indeed, of any sensitive surface employed in picture making—but the benefit of the fineness of the ultimate grains should not be unduly laboured to the exclusion of other conditions.

Renwick (Relation between Sensitiveness and Grain Size in Photographic Emulsions, Photo. Journal, 1921, lxi. 333) considers that there is no direct relation between grain size and sensitiveness, and remarks 'as to whether only a limited range of sizes is possible for a given sensitiveness, and conversely, I have still an open mind. . . . All the evidence I have seen goes to show that grain size and sensitiveness are not mutually interdependent qualities, though, in practice, we have not yet learned how to vary them independently. The potentialities of an emulsion, its possible optimum speed, its density-giving properties, and its grain characteristics are largely and possibly completely determined at the instant of mixing the reagents. Undue stress has, I think, been laid upon the subsequent stages of the processes of emulsion making which merely bring these potentialities to fruition; they are, indeed, in the true sense, "ripening" processes and little more.' Sheppard (The Modern Chemistry of Gelatine, Research Laboratory, Eastman Kodak, *see* J. Ind. Eng. Chem. 1922, xiv., and Brit. J. Photo. 1922, lxix. 677) states that 'Heating suspensions tends to agglomerate the particles and lessen the dispersity, and since negative emulsions are "ripened" by heat to increase their sensitiveness and density-giving power, it has, therefore, been supposed that high-speed negative emulsions, with coarse grains, simply represent a stage produced from fine-grained emulsions by heat treatment and Ostwald ripening. This is not the case. The conditions in the preparation of the coarser-grained "high-speed' emulsions are different, and, in particular, the concentration of the reactants is higher, and that of the gelatine is lower' (*see* also A. P. H. Trivelli and S. E. Sheppard, The Silver Bromide Grain in Photographic Emulsions, van Nostrand, 1921; and T. Svedberg, Zeits. wiss. Photo, 1920, xx; Photo. Journal, 1921, lxi. 325–332; *ibid.* 1922, lxii. 183–192).

This proportional dispersity of the grain determines, to a considerable extent, the range of gradation that can be rendered by a given emulsion, though this is not the sole determinant. The simplest case is that of a 'slow' emulsion made for the production of negatives of black-and-white subjects, the so-called 'process' plates made for photo-mechanical purposes (*see* Slade and Higson, The Emulsion for a Process Plate, Photo. Journal, lix. 260). In such a plate the grains are fairly uniform in size and the *characteristic curve* of the plate (*see* this article, 'The Hurter and Driffield' system) is steep in character. If the grains in a plate having this property be compared with those found in a plate made for the representation of a more extended scale, say a plate made for portraiture, it will be found that the particles are more varied in size and the characteristic curve of this type of film will be flatter, being a summation of the curves due to each degree of dispersity. In practice the production of a film capable of rendering an extended scale is due to blending of different emulsions in suitable proportion. So far it has been assumed that the emulsion contains only silver bromide, but either silver iodide or chloride may be emulsified in gelatine. The use of silver iodide was originally suggested by Penny (1877), and its use was first fully studied by Abney (1880), who advocated its employment. Silver iodide may be emulsified direct or may be produced by treating an emulsion of silver bromide by an alkali iodide, but an emulsion of silver iodide is comparatively insensitive compared with one of silver bromide. If emulsions of the two halides after washing be mixed, then a different result is obtained. The combined emulsion is less generally sensitive than one of silver bromide alone, and its spectral sensitiveness is more confined, being lower to the less refrangible end of the spectrum. Plates prepared in this manner are generally more opaque than plain bromide plates, and in consequence do not suffer so much from the effects of one form of halation (*q.v.*), they show less the harmful results of unduly prolonged exposures, and permit, in consequence of their lower sensitiveness, the use of a brighter light during development. The conversion of the silver iodide to a soluble salt by the action of sodium thiosulphate used in fixation is slower than the similar action with silver bromide, which results in this operation being more prolonged in the case of plates prepared with both salts than with pure silver bromide films. It is assumed often that plates prepared with silver iodide yield negatives having greater 'brilliance,' to use a commonly understood technical term, but this quality, if it be really a result, may be regarded as being due to the effect of certain characteristics mentioned, rather than to any specific property of the salt, to show a different scale of gradation. It would appear that silver iodide when present in a bromide emulsion acts to some extent as a restrainer during the process of development, and this tends to the production of contrast. Gelatine itself acts in a similar manner when present in excess, although to a much less degree.

Eder has discussed the phenomenon, and has pointed out that the addition of an undigested silver bromide emulsion to one highly ripened corrects any slight tendency of the latter to give 'fog.' This effect of iodide is not shown in emulsions when the silver iodide and silver bromide are formed together in the same emulsion, now the common practice, for under this condition a silver bromo-iodide appears to be formed, and this emulsion shows different properties. The change which ensues on digesting a silver halide in gelatine may be brought about by other means. In 1877, Johnson (Brit. J. Photo Almanac, 1877, 95) suggested the addition of ammonia to the emulsion, and

in 1879 Monckhoven (Photographische Correspondenz, xvi. 197) stated that upon heating an emulsion with the addition of ammonia for some hours the same gain in sensitiveness was brought about that followed a digestion in the neutral emulsion for several days. The original method of Monckhoven consisted in the addition of 5 c.c. of ammonia (sp.gr. 0·910) to every 300 c.c. of emulsion before digestion, but a tendency to 'fog' was found. The conditions under which ammonia could be used with advantage were fully investigated by Eder, who showed in addition that ammonium carbonate and sodium carbonate would increase the ripening process even in the cold. From these investigations arose the so-called 'ammonia process,' which became the alternative to the 'boiling process,' and is now largely used in the commercial manufacture of dry plates, although the precise form of the ammonia method now adopted may be said to be a combination of the two systems. In the process of Eder the silver bromide was formed by the addition of ammonia-nitrate of silver to a bromised gelatine, after which the emulsion was maintained for a brief period at a temperature of 35° and then allowed to cool to 24°C. It was found that the emulsion gave fogged plates if the temperature during the digestion were allowed to exceed 40°C. The 'insensitive' form of the halide is by this treatment converted to the 'sensitive' modification—the terms are relative—in a brief space of time even at the lower temperature stated, and no gain in sensitiveness arose from a longer digestion than 30 minutes. No 'fog' ensued when the digestion was prolonged to 3 hours if the temperature did not exceed the limit given. If the temperature rose or an excess of ammonia was used, then hydrolysation of the gelatine took place, the emulsion, in consequence, became less viscous, aggregation of the halide took place with separation of the salt, and the emulsion yielded coarse grained images.

The washing operation, by which the saline products of decomposition are eventually removed, must with an emulsion prepared by this method be conducted with care, any appreciable residue of the excess alkali halide reducing 'speed,' and the presence of residual ammonia impaired the keeping qualities of the plates. The precaution with respect to the temperature of digestion was the more necessary, as in this method the whole mass of the gelatine required is present in the emulsion during the digestion, and not as in the case of the plain boiling method, when a portion of the gelatine only was used in the emulsification, the remainder being added later.

A modification of the ammonia process of a more complicated character was later introduced, in which the emulsion of the silver salt found by precipitation in neutral solution was, after digestion for half an hour, between 60°–100°C., cooled to 21°C., and then received an addition of ammonia, and subsequently digested for half an hour at a temperature of 38°C., when it was then allowed to set and finally washed. Provided that the emulsion was not digested at a higher temperature after the addition of ammonia than that stated no harm ensued, and the ultimate value with respect to speed would be reached with more certainty. Indeed, had the maximum speed producible on boiling, under the conditions which obtained, not been reached, the more prolonged digestion with ammonia might be relied upon to complete the change. The whole of the gelatine required was used in the emulsification as in the former process, and the same care was observed in the subsequent washing. According to Eder there was a slight gain in sensitiveness by adopting the second plan, and it was found that the plates possessed a better scale of gradation. In the light of modern investigation this difference may be regarded as being due to the greater dispersity of the silver halide. Abney during his experience in working this method appears to have found that if the silver nitrate were added when the bromised gelatine was at a temperature of 60°–70°C. the highly sensitive form of the halide was more readily produced, an observation in conformity with the later experience of other emulsion makers.

Other early workers, as for example, Cowan, developed methods for emulsification at lower temperatures, to which processes the term 'cold' emulsification was applied. Cowan formed the silver halide by the addition of the bromised gelatine to an ammoniacal solution of silver nitrate at a comparatively low temperature when a fine emulsion was formed, and then added the remaining gelatine in the form of a cool aqueous solution. After shaking the emulsion was allowed to set, and was then kept 12 hours, after which the jelly was washed. In this method the ripening is effected by the aid of the ammonia in a slightly viscous solution in the short period which elapses before the final quantity of gelatine necessary to form a firm jelly is added. It was found that the ripening took place more quickly by this plan than if the whole of the necessary gelatine were present during the precipitation, in which event a raising of the temperature (which had the result of reducing viscosity apart from other effects) was necessary to accomplish ripening in a comparable time.

Some of the early emulsion workers sought to avoid emulsifying in gelatine by precipitating the halide under other conditions. Abney (Photography with Emulsions, 1855, 107–110) precipitated silver bromide in water by the addition of the halide to the silver solutions, alternately quota by quota, the silver nitrate being in excess. The finely divided silver bromide is then treated with nitric acid to prevent any subsequent tendency to 'fog' in the emulsion, and eventually washed by decantation with water until all traces of free silver nitrate and nitric acid have been removed. In all probability some minute trace of silver nitrate remains adsorbed to the halide, as experience has proved that it is very difficult to remove the last traces of silver nitrate from halides precipitated in the presence of an excess of the silver salt, and to this trace some of the sensitiveness of the emulsion was possibly due. An emulsion so prepared, as Eder originally pointed out, would be slightly more sensitive than a similar emulsion made with an excess of alkali halide. Abney observed that a *slight* digestion increased the speed. Eder, commenting (Modern Dry Plates, English Trans. 1881, 11) upon some experiments by Szekely, who

followed Abney's method, stated that there was an increase in intensity, by which is meant ability to yield density on development and an increase in grain size, but that silver bromide precipitated in this way must not be considered as more sensitive than one prepared with excess of alkali halide, because the contrary was actually the case. The silver bromide after washing was then treated with gelatine solution, when the halide is taken up forming an emulsion which after thorough mixing and filtration was ready for plate coating. Abney states, by this method of forming the silver bromide the precipitate will be so fine that it will often require a couple of days for settlement in the precipitation vessel, but that the deposition (which was necessary before washing could be effected by decantation) could be accelerated by raising the water containing the suspension to the boiling-point. When coagulation took place, Abney stated that the coagulation does not signify, since if the particles have once been precipitated in a fine state of division they will separate in the subsequent operations, viz. when mixed with the gelatine solution. This statement is interesting, especially in view of observations of Eder (Handbuch der Photographie, 1902, III, 28), that the peptonisation of silver halides precipitated in aqueous solution depends on whether the silver salt was precipitated in the presence of excess of silver or of halide. In the case of the halide precipitated in the presence of excess of halogen salt, some of which remained adsorbed to the silver bromide, even after careful washing, the latter is peptonised on treatment with a warm solution of gelatine with the consequent formation of an emulsion. With respect to the halide precipitated in the presence of excess of silver nitrate this peptonisation does not take place. Furthermore, in this change the bromine ions formed by dissociation of the adsorbed alkali bromide play an important part. But by treating the precipitated silver salt in the aqueous solution before the addition of the gelatine (as in Abney's accelerated washing process) the halide is altered so that it will not peptonise.

As to the character of the emulsion produced by this method, Luppo-Cramer states (Photographische Correspondenz, xliv. 578) that it is possible to make a very fine grained but not a colloidal emulsion.

Later, Abney modified his process by introducing glycerine to the aqueous solution of silver nitrate in which the halide was precipitated by the addition of the alkali bromide, employing for this purpose, water 8, glycerine 1, by volume, and proceeding in the same manner as in the earlier method. It is stated that emulsions prepared by the plain-water process gave films 'which, for rapidity, will bear comparison with any other process' (Abney, Photography with Emulsions, 1885, 110). It should be remembered that all comparisons as to speed by the early emulsionists were made primarily with reference to collodion processes, and that rapidity of the plates then obtained would be of very low value as compared with the products of to-day.

From these different methods it would appear that the presence of a solvent of silver halide is necessary in order to promote the ripening process. Whether it be an alkali halide or ammonia the transformation takes place. In the case of the former a relatively elevated temperature and more prolonged action is necessary, whereas in the presence of the more energetic solvent of the halide, the ammonia, a lower temperature and more brief digestion suffices. Whatever be the conditions of the final treatment, it must be recognised that the conditions of the initial stage, the emulsification, profoundly affect the character of the final sensitive complex. Any subsequent ripening is, after all, only a continuation of that process which commences with the first precipitation of the halide salt, the same influences are at work to a greater or less degree from the first.

Emulsification in gum arabic (with gelatine eventually added as a binder) was advocated by Mawdsley in 1879 (Brit. Jour. Photo. 1879, 398), and Bruyere in 1881 (Year Book of Photography, Photo. News, 1881, 145), and Ritchie proposed and patented the use of 'Arabin' for the purpose (*see* Editorial note, Photo. News, 1880, 85). Eder, criticising the process (Modern Dry Plates, English Trans. 1881, 15), observed that if the emulsification took place in the cold the sensitiveness was inferior to that of a gelatine emulsion, and that when emulsified with heat or with the addition of ammonia an increased sensitiveness was obtained, yet the plates showed such a tendency to frilling and expansion of the films that 'this proceeding appears to be impracticable.' This frilling, due to the presence of a highly soluble body, the gum arabic, not removed in the subsequent washing, was a real defect, and was similar to that produced by the presence of gelatine which had lost its setting power by digestion in an emulsion prepared by the boiling process. In the latter case the removal of such gelatose and gelatone was one of the arguments in favour of 'washing' an emulsion by centrifuge, because by that method practically the whole of the original gelatine was removed, the halide being eventually emulsified in fresh gelatine solution which had not been subjected to the destructive action of heat. Luppo-Cramer at a later date (Eder's Jahrbuch der Photographie, 1904, xxiii. 436), when our knowledge concerning emulsions was more extended, investigated the emulsification of silver bromide in gum arabic, and found that the product was much less sensitive than when gelatine was the emulsifying medium, thus confirming Eder's conclusions. A similar conclusion was formed with respect to cascin.

An investigation into the possibilities of silicic acid as an emulsifying agent was made by Schaum and Schloemann (Zeitschrift fur Wiss: Photographie, 1906; Photographische Correspondenz, xliii. 406), following some experiments made by C. A. Lobry de Bruyn (Rec. Trav. Pay Bas et Belgique, 1900, xix. 236). The emulsion was prepared by adding a solution of potassium bromide in colloidal silicic acid carefully purified by dialysis to a similar solution of silver nitrate. The emulsion after standing half an hour was carefully filtered and then coated on glass, and the coated plates allowed to stand until the film 'gelled,' after which the film was carefully washed in water to remove the excess of soluble halide. The film must be used moist, as in drying it leaves the

glass, a feature not avoided by the use of a substratum. Development was effected by means of ferrous oxalate, and the authors record that the speed tests showed a rapidity equal to about 1/45 that of a 'Hauff transparency plate,' which indicates a very low value.[1] In view of the fact that the medium differs from all organic media employed in emulsion making in being, so far as we know, chemically inert, the experiments are of decided interest, as the plates afford an additional aid to the study of the formation of the latent image, but further investigation in the direction of the use of the plates for this purpose appears to have been suspended. The employment of *agar agar* (Alga: *Geledium corneum*), as an emulsifying agent, has been studied by Cooper and Nuttall (Photo. Journal, 1908, xlviii. (new series xxxii.), 11), who have shown that it is possible to emulsify silver bromide in this medium and to obtain plates possessing a fair speed. The alga has been used as a medium in the production of sensitive papers for print-out images where silver chloride with organic salts of silver form the sensitive compound. Albumen has been proposed as an emulsifying agent for 'print out' and development papers for positive making by E. H. Farmer (*see* Silver Gold Albumen Process, Patent Abs. No. 524, Jan. 12, 1888). Lehmann and Knoche (Brit. J. Photo. 1914, lxi. 759, 790) have investigated the possibilities of albumen emulsions with especial reference to ripening without increase in halide grain size.

It would be an exclusion not in any way justified to disregard the changes which occur in the gelatine itself as influencing speed. All attempts to produce highly sensitive emulsion films in the sense understood to-day by the agency of other emulsifying media, as collodion, gum arabic, agar agar, starch, casein have failed, and the conclusion, therefore, must be that there is an inherent property in the gelatine, quite apart from its suitability as a medium, which makes possible the dry plate of to-day with its high speed and power of rendering an extended scale of gradation of light and shade. So far little has been published as to the part played in this effect by the cleavage products of the gelatine, but that these do play an important part there can be little doubt.[2] The processes adopted for ripening are precisely those which bring about to a greater or less degree the cleavage of gelatine. Although the possible benefits of this hydrolysis do not appear to have been recognised by the early emulsion makers, they were alive to its inconveniences, the lowering of the melting-, and the consequent raising of the setting-point, the loss in viscosity, the lack of firmness in the jelly, and the tendency to 'fog' owing to the presence of the products of hydrolisation, were drawbacks of moment in practical plate making. The lack of firmness in the jelly causes difficulty in washing the emulsion, the lack of viscosity leads to 'settling out' of the halide with consequent tendency to a less homogeneous film. This separation when accompanied with a high setting-point means that the plates take an undue time to set on coating, and the 'settling out' tends to produce lack of adhesion and consequent undue proneness on the part of the film subsequently to frill and leave the support. In consequence the practice of emulsifying in a small portion of the total gelatine required, and after the digestion adding the remainder, first proposed by Bolton in 1873, was an important step in practical emulsion making. A high gelatine content in an emulsion, amongst other drawbacks, tends to prolong the necessary washing before coating, and it introduces difficulties in the subsequent use of the plates for negative making. Reduction of the gelatine content below a certain amount leads to a lessened speed.

For the production of maximum contrast combined with sharp definition of the elements of the image the wet collodion process has not been equalled by the gelatine dry-plate method. Images of this character are required in certain branches of photo-mechanical work, viz. for line reproduction and for 'broken tone' (dot) images made by the translation of continuous tone pictures by means of the ruled screen (*see* Photo-Mechanical Processes). For this purpose the so-called 'process dry-plate' is employed, which is essentially a plate yielding high density upon suitable exposure and development with an abrupt scale of gradation, and a plate of this character fulfils the requirements. In order, however, to be entirely satisfactory the film must be thin and the gelatine content low. Some process plates, whilst yielding the necessary density of image and contrast, do not fulfil the other condition, and in this respect fail to respond to the necessities. Here then is an important instance of the influence of the ratio of gelatine to halide and film thickness. A further example of the influence of the gelatine content is seen in the plates of Schumann (Ann. Physik. 1901, v.), produced for the purpose of spectrum photography in the region of the ultra-violet where the gelatine is reduced to an extremely low quantity. By means of the Schumann plate it is possible to make negative records beyond 185$\mu\mu$, which would not be possible with ordinary gelatine dry plates, owing to the absorption of gelatine which becomes very pronounced for regions beyond 220$\mu\mu$. Incidentally, the 'resolution' (*see* p. 225) of such plates is high.

Another process for preparing plates suitable for producing spectral records has been described by J. Duclaux and P. Jeantil (J. de Physique, 1921, ii. 156–159), in which ordinary dry plates are treated in a horizontal position with 4-N-sulphuric acid, by which the gelatine is dissolved and the silver halides settle out, the dissolved gelatine being removed by careful water washing, after which the film is dried and is then coated with a protective covering of plain collodion. The investigators state that the film is very sensitive to ultra-violet radiations, recording beyond 190$\mu\mu$.

The image yielded by an ordinary bromide emulsion developed by a non-staining developer

[1] According to Renwick (Photographic Images, Visible and Invisible, Hurter Memorial Lecture, J. Soc. Chem. Ind. 1920), 'very sensitive emulsions can be prepared in colloidal silicic acid.

[2] H. Müller has proposed the addition of pepsin-hydrochloric acid to a plate emulsion for the purpose of producing plates having a steep gradation (D. R. P. 313180, 1918; *see* J. Soc. Chem. Ind. xxxviii. 878*a*, 1918). The effect of this combination is to convert a portion of the gelatine (α) to gelatose (β), according to the length of time (and the temperature) during which the enzyme is allowed to act.

is a neutral grey, but for certain purposes coloured images are desired, as for example, positives for lantern projection, where a relief from the ordinary neutral tint is pleasurable. Emulsions made with chloride of silver are admirably adapted for this purpose, and yield, with suitable exposure and development, colours as widely diverse as olive-green and crimson when examined by *transmitted* light. Such emulsions are characterised by fine grain, extreme transparency, and very low speed. As well as chloride, silver chloro-bromide emulsions are used for the same purpose. They have the advantage of higher speed and longer scale of gradation, and the range of colour obtainable by suitable exposure and development is considerable, though it is not possible to produce certain of the colours by direct development which are yielded by plain chloride emulsions. The production of coloured images on silver salts by development upon an opaque or translucent support for viewing by reflected light is not quite so easy. Nietz and Huse (Brit. Journ. Photo. 1917, 497; Abridged Scientific Publications, Research Laboratory, Eastman Kodak, No. 53, iii. 16) have investigated the conditions for the production of coloured images on silver chloride emulsion upon paper by development, using chlorquinol as the reducing agent in the presence of sodium sulphite and carbonate, and potassium bromide and metabisulphite. They find that by suitable conditions of exposure and development hues passing through the stages yellow, yellow-brown, red-brown, sepia to greenish-black, are possible. The hue is due simply to the state of division of the silver, and the production of any desired colour within the series obtainable depends upon the careful adjustment of all the conditions specified in their communication.

For the influence of the state of division of the silver upon the colour of photographic image, *see* Chapman Jones (Photo. Journal, lii. (new series xxxvi.), 349–356), and also F. Formstecher (Deutsche Opt. Woch, 1920, 33), who confirms the contention of Chapman Jones, that the image colour is dependent on the size of the silver particle.

Emulsions of citro-chloride of silver in gelatine (or collodion) have been used for certain types of positives where the image is obtained by direct exposure and not by exposure followed by development. In the production of positive prints by exposure and development, bromide papers are now enormously used, and whilst the predominant tone is black or grey, there has always been the desire for images of a brown or sepia colour which have been up to comparatively recently, made by a toning process which consists in converting the silver image to silver sulphide, when the physical condition of the primary image and the mode of conversion determined the precise hue which is obtained. But this *modus operandi* has not been entirely satisfactory, and emulsion makers for many years have devoted some part of their attention to endeavouring to produce emulsions which would yield warm tones on development, and these emulsions have principally a bromo-chloride of silver as their sensitive salt. Chloride of silver emulsion in an unwashed or washed condition constitutes the sensitive substance in the so-called 'gas light' papers, and these are employed in photography to a considerable extent.

In a certain form of emulsion, as that for the purpose of X-ray photography, considerable opacity is necessary, in order to produce the maximum absorption of the radiation, and the silver content is high. The physical condition of the halide must be such that it yields density readily upon development. Such emulsions were often in the earlier days of production of low speed to ordinary light, but the modern X-ray plate or film is reasonably fast to light. For the purpose of increasing the effects of the radiations fluorescent screens are employed. For this purpose the property shown by calcium tungstate to fluoresce under the radiations from an X-ray tube is used. The material in a crystalline condition is powdered and coated, using a suitable binding medium, upon a support which has only a slight absorption for the exciting radiation. This screen is used in contact with the sensitive surface, exposure being made through the fluorescent screen or through the emulsion film. The light emitted by the screen under the influence of the radiation from the X-ray tube was found in a certain instance to extend from 360$\mu\mu$ to 520$\mu\mu$, and this region is in good correspondence with the regional sensitiveness of many X-ray films (*see* M. B. Hodgson, Phys. Rev. Dec. 1898; and Abridged Scientific Publications, Research Laboratory, Eastman Kodak, iii. No. 67, 90–91).

To avoid the use of the screen, emulsion coated papers have been prepared, in which the emulsion rests upon a film of calcium tungstate (E. H. Burnett, J. Soc. Chem. Ind. 1919, 389a). Another expedient is to add to the emulsion soluble transparent substances (Mutscheller), which have no influence upon the halide by their mere presence until the film is subjected to the X-ray radiation, when they fluoresce and increase the photographic effect. The drawback to contact agents is a possible impairment of the keeping qualities of the emulsion film.

Interesting efforts have been made by additions to the emulsion, or by treatment of the finished plates before exposure, to combat the results of unduly prolonged light action, which produces reversal of the normal effect, viz. the phenomenon of a positive image appearing instead of a negative on development. For this purpose W. H. Caldwell has employed salts or derivatives of hydrazin and of hydroxylamine (*see* E. Sangar Shepherd, Photo. Journal, 1911, li. (new series xxxv.), 249–257; and Discussion, *ibid.* 1913, liii. (new series xxxvii.), 15–20). Crowther has used for the same end derivatives of *p*-phenylene diamene (Crowther, E. Raymond, Photo. Journal, 1914, liv. (new series xxxviii), 250–260).

All additions to emulsions made for any purpose other than a modification of speed should, however, be considered in the light of the possible influence on that factor, for an advantage in one direction may be gained by a loss in another, and although high speed is not in all cases a quality of great importance, and may in some be a detriment, yet its possession is desirable in the majority of instances in negative making in practical everyday

photography. Many substances when added to the emulsion or to the coated surface increase the speed, others act in the opposite direction, using the term 'speed' in the sense understood by Hurter and Driffield (*q.v.*). Cupric, ferric, mercuric, and uranic salts, and, usually, acids, lower speed, whilst many basic and alkaline bodies enhance the speed. A lessened speed by an addition to the emulsion may be due to a retardation of the ripening, and oxidising agents so act, whilst an enhancement of the speed might be expected to follow from the addition of any agent, for example, that would act as a solvent of the silver halide, as, for example, ammonia, which would facilitate ripening.

The term 'washing' an emulsion is applied to the process whereby the soluble salts are removed. If this be not done, then in an ordinary emulsion crystallisation would alter the structure of the film, and the surface crystallisation would prevent image formation, and furthermore, the excess alkali halide remaining would reduce the speed enormously. So far as preventing the crystallisation, that could be done by retaining the salts in solid solution by an excess of gelatine, and this plan is followed with certain types of emulsion used in coating sensitive papers, but the practice is not admissible for plate emulsions.

There are three forms of operation by means of which the soluble salts may be removed—

(*a*) By osmosis.

(*b*) By precipitation.

(*c*) By centrifuge.

(*a*) This is the original, and the method now almost wholly used. The jelly, finely shredded, is washed in water at a low temperature until the soluble bodies are removed, when the emulsion shreds are carefully drained before remelting. It is this form of washing which demands a certain percentage of gelatine, in excess of the quantity required for emulsification, because water washing would be impracticable if the gel were not reasonably firm. It has been held that the whole of the soluble halide must be removed, but this is a question of degree, and, moreover, no rapid emulsion would work 'clean' in development in the absence of free bromide. In practice a certain quantity is always added in the final stage before coating.

(*b*) The centrifugal method was advocated and employed at one period in plate making, but has been abandoned, and experiences during its employment were varied. It had the one great advantage of removing the whole, or practically the whole, of the original gelatine, and plates prepared from such emulsions have a lessened tendency to 'fog' and to frill. The most complete published account of the use of the centrifuge was given by Baekeland (Int. Kongress Angew. Chemie, 1903, iv. 11) who, as an experienced emulsion maker, spoke favourably of its employment, observing that emulsions 'washed' in this manner possess the advantage of having always the same chemical composition, which does not obtain in the case of water-washed emulsions, which may retain various proportions of soluble salts and ammonia, together with 'undefined' products of partial destruction of gelatine. It is not likely in the practical emulsion making of to-day that there will be hydrolised gelatine in the condition and to the extent that induces 'fog,' and the influence of such does not appear to be permanent, for if such gelatine be removed and replaced by new gelatine the effect found in the reverse of this operation is no longer apparent. This fact appears to have been noticed by Burton (Handbuch der Photographie, 1902, iii. [i.] 39), who observed that when an emulsion gave green 'fog' ('dichroic fog'), owing to long digestion was treated so as to remove the gelatine and then re-emulsified in a fresh portion, the defect disappeared and satisfactory plates were produced without loss of sensitiveness.

(*c*) If into an emulsion to which the final gelatine has been added there be poured alcohol, eventually the gelatine will be precipitated as a clot which will contain the silver halide, the soluble products remaining in solution. The clot is rinsed with alcohol, broken up and allowed to swell in water, and the jelly is then melted and made up to volume by the addition of water. This method was introduced by Wratten in 1877, and was commercially employed. It is an effective method but is expensive, and its use has been abandoned in favour of water washing. It is, however, a useful and rapid plan for experimentalists who desire to make small batches of emulsion.

The support for the emulsion may be glass, celluloid, or paper, but the latter is now only used for emulsions intended for print making. The advantage of celluloid lies primarily in the fact that this support can be rolled, and thus may be employed in rollable film cameras, and for this purpose is employed to an enormous extent. Celluloid as a support was first introduced by Parkes in 1856. Emulsion-coated celluloid was introduced by Carbutt (U.S.A.) in 1884. The modern development of the celluloid-coated film is, however, entirely due to Eastman (Kodak). Celluloid in cut films to be used in place of glass plates has been used for many years, but recently has come to the fore, and is now to a considerable extent replacing glass.

All negatives made on emulsion films suffer from the defect of halation (*q.v.*), which briefly may be defined as an extension of image boundary beyond that of the optical image on the plate surface at the time of exposure. One form of this extension, viz. 'reflection' halation, is due to the transparent support, and varies in amount with its thickness, which, owing to practical necessities, is always greater on glass than in celluloid, with consequent increase in the area of the defect. Many photographers are alive to the serious lowering of quality that ensues from halation in its several forms, and, in consequence, the advantage of thin supports which the use of celluloid permits is appreciated, and the employment of films in cut form is likely to increase.

To secure the adhesion of the emulsion film, which in the processes of development, fixation, and washing of negatives tends to leave the glass, some preliminary coating of the support is, in general, practically a necessity. This coating or substratum in the case of glass is generally a dilute solution of gelatine containing chrome alum, which renders the gelatine insoluble on drying; but the problem in

the case of celluloid is not so simple, for the surface of the celluloid is naturally repellant. The nature of the substratum used in a particular ease is not generally known outside the factory, but a solution of gelatine eontaining chrome alum and acetone has been recommended for the purpose.

The expulsion of water, the final drying of the film on the support, is a very important feature in plate making. Plates are dried in chambers by means of a current of filtered warm air, which has previously been freed from moisture by passing over pipe staeks through whieh a flow of brine at low temperature is maintained. The freezing of the water on the exterior of the pipes dehydrates the air which passes forward to be warmed. The current is regulated to permit the drying to take place in a eertain time, and the operation once started must suffer no check.

The substance Gelatine (*q.v.*) upon which the emulsion maker depends is a body, regarding which knowledge is slowly accumulating, but there remains much to be elucidated with respect to its properties for photographic emulsion making. Much valuable information —colour, reaction, ash, freedom (or reverse) from SO_2 and sulphites, hardening agents, antiseptics, fat, absence of bodies reducing ammoniacal silver nitrate, absorption of water, viscosity of a 'solution,' gelling (freezing, setting) temperature of a 'solution,' melting-point of a gel of definite 'concentration,' content of non-gelling bodies as gelatose, gelatone, and other products[1] of the hydrolysis of the original collagen—to take only the simple aspects, with respect to a particular sample of gelatine may be ascertained by careful investigation in the laboratory, but the eonnection between these and the behaviour of the particular gelatine when employed in actual emulsion making is not so apparent. The bearing of particular properties is only approximately established, and in some instances is only a eonjecture. Still less has been explained as to the effect of the particular chemical entities that result from the digestion of the gelatine—gelatose, gelatone, and amino aeids—upon the final eharacter of the emulsion. The regular production of particular types of emulsion is to a great extent a matter of eareful and systematic procedure founded upon long and continual experience. In respect to the physical and chemical properties of gelatine in relation to their bearing upon photographic emulsions, the following statement of Storr is of considerable interest:—

'Apart, however, from the fact that certain minima of strength—setting-power, viscosity, &c.—are necessary, and that a stronger gelatine is easier and more economical to work, it is the writer's experience that the physical properties are a very insufficient guide to the suitability of gelatine for making photographic emulsions. There are certain chemical differences between different types of gelatine and even between different batches of the same type, which are more effective than are the physical properties in determining speed, freedom from fog, and such qualities in different types of emulsion. As to the exact nature of these chemical differences there are very few available data, but it is very possible, if not probable, that they are due to the presence or absence of very small quantities of specific substances, rather than to variations in the proportions of the main constituents of the gelatine. A process such as washing the gelatine, for instance, will improve it for some purposes and spoil it for others. The final test of the photographic manufacturer is therefore in the particular emulsion for which the gelatine is required, and the safeguards of the gelatine manufacturer are care in selection of raw material and in its treatment' (B. V. Storr, Annual Reports, J. Soc. Chem. Ind. 1918, xxxvii. 465; *see also* S. E. Sheppard, Gelatine in the Photographic Process, J. Ind. Eng. Chem. 1922, 1025).

A valuable Bibliography of Gelatine, compiled by the labours of Dr. T. Slater Price, has been issued by the British Photographic Research Association (First Report of the Adhesives Research Committee, Dept. Scientific and Industrial Research, H.M. Stationery Office, London, 1922).

The most complete and comprehensive account of the chemistry and physics of photographic sensitive surfaces with silver salts is to be found in the writings of Bancroft (W. D. Bancroft, The Photographic Plate, J. Phys. Chem. 1910, xiv.–1913, xvii.). These contributions are a mine of information on the theoretical and technical aspects of this branch of photography, and constitute a critical epitome of the subject to their date. It is, however, observed that some of Bancroft's conclusions have been disputed, and they should be read in the light of recent work. The more modern types of emulsion differ from those reviewed by this author, and his conclusions in some respects do not apply to many of the high-speed products of to-day.

Practice.—Reference has already been made in the historical introduction to the original experiment of Maddox which led to the gelatine dry plate. Although several experimental photographers devoted their attention to the making of emulsions after Maddox published his first attempt, notably Abney, Eder, Warnerke, England, Kennett Van Monckhoven, Bolton, Wilson, Wratten, Eastman, Burgess, some of whom eventually became makers of dry plates commercially, it should always be recognised that the dry plate in its present state is the outcome of careful work and experience in commercial dry plate factories. Few secrets are so carefully guarded as those which lie in the methods adopted, for whilst to make experimentally a small batch of emulsion which will yield dry plates of moderate speed and fair gradation is not difficult, as, indeed, many independent workers have demonstrated, it is quite a different problem to produce day after

[1] It should be remembered that in the preparation of gelatine by the cleavage of collagen (complex in tendons and skins) or ossein (complex in bones) the final product is in all cases the result of progressive hydrolysis, and so varies in state. Before the whole of the parent body has been broken down some of the first-formed gelatine (α) has been converted to gelatose (β), and later this passes by the continued hydrolysis to gelatone (γ), so that the final product is a mixture of the entities that these terms represent. It is true that an endeavour is made to produce gelatine only as far as may be practicable, but the fact remains that a number of the highest grade gelatines contain gelatose and gelatone.

day large quantities of emulsion of different types which, alone or on blending, will give plates of the different characteristics necessary in photography of various kinds and, moreover, to maintain these qualities regularly in the output with that constancy expected by the user.

Since the dry plate is the foundation of modern photography, precluding the possibilities of a total change in method, of which there is at present no indication, the study of emulsions and their behaviour in the form in which they are used is a matter of fundamental importance, and it is questionable whether any other branch of photographic technology affords a field equal in its interest. Whilst many important problems requiring solution may be studied by the aid of dry plates available in commerce, it will be found that others require a study of the emulsion *ab initio*. In view of the fact that many of the more important properties of emulsions, the nature of which are now common knowledge, were the outcome of the labours of the early photographers, there is nothing in the fact that commercial manufacture of dry plates of high quality requires considerable knowledge and experience to deter the private investigator from adding his quota to the literature of the subject. For the preliminary assistance of those who may be interested in the problem a method is given for the making of an emulsion, which will be of low speed, and this may serve as a starting-point. It is found that the manufacture of small batches of emulsion tends to produce differences which are somewhat puzzling to the experimentalist, and as the uniformity of one batch with its successor is important it is recommended that quantities of not less than 1000 c.c. be made. Emulsion making is thus somewhat expensive, and care should be taken of all residues, from which the silver should be recovered.[1]

The gelatine used should be the finest procurable made for emulsion purposes, and two varieties are necessary, technically designated 'soft' and 'hard.' The salts employed should be 'pure.'

(*a*)	Potassium bromide	34 grams
	Potassium iodide	2 ,,
	Gelatine ('soft')	10 ,,
	Water (distilled)	325 c.c.

The gelatine is allowed to swell in a portion of the water, sufficient being retained for solution of the salts. The gelatine mass after swelling is heated until a melt is produced, when the solution of the halides is added with thorough mixing.

(*b*)	Silver nitrate (triple cryst.)	21 grams
	Water (distilled)	325 c.c.

[1] The recovery of residues is an important item in the conduct of an emulsion factory. When the concentration of the residues is high economical recovery is not difficult, but this does not generally obtain when the silver salt present is low. To meet the latter difficulty Renwick and Storr have proposed and patented (Eng. Pats. 16708 and 102168, 1915; and J. Soc. Chem. Ind. 1917, 47) a method for the recovery of silver from dilute gelatine emulsions, one of which depends on the network of gelatine and a colloidal hydroxide, which is produced by the dilution of a metallic salt in a slightly alkaline bath. The action does not take place when fresh gelatine is involved, nor when the solutions are above a definite temperature. Several methods are given in the Patent Specifications, to which reference should be made.

(*c*)	Silver nitrate, powdered	21 grams
(*d*)	Gelatine (hard and soft in equal parts)	80 ,,

Heat (*a*) and (*b*) to 50°C. and emulsify by adding (*b*) to (*a*) in a steady stream, stirring the whole of the time, the initial additions being the most important. Afterwards add in a gentle stream, stirring well and regularly, the remaining quantity of the silver nitrate (*c*) in powder. Cool the emulsion to 43°C. and then add *slowly* 5 c.c. of ammonia (sp.gr. 0·880), during which addition the emulsion is kept stirred. Digest for 30 minutes at 43°C. and then add the gelatine (*d*) in *small* pieces, and stir until it is dissolved, after which set off, standing the containing vessel in cold water, stirring occasionally. Allow to stand for 24 hours, shred into small pieces and cover with water, allowing 2 litres. Stir. Change water 8 times, allowing 20 minutes for each change. Drain carefully and thoroughly after washing, on clean grease free fine cotton canvas (Wratten and Wainwright, Year Book Photo. 1878). ('Woolwork' canvas answers well.) Collect washed shreds and melt, heating gradually to 50°C., stir well and make up the bulk to 1000 c.c. with distilled water at the same temperature, and when mixed add—

Alcohol	35 c.c.
Thymol (5 p.c. in alcohol)	2 ,,
Potassium bromide (10 p.c. solution)	5 ,,
Chrome alum (5 p.c. solution)	10 ,,

Thoroughly mix and filter. Allow to stand 30 minutes when the emulsion is ready for coating.

The whole of the operations from the emulsification must be conducted in a 'safe' dark-room light. Glass vessels should be employed and perfect cleanliness is essential. Uniformity of procedure with successive batches is necessary for constancy in result. Emulsions in the 'gel' form will keep in good condition for a reasonable time in the presence of the thymol if maintained at a low temperature, say, between 5°–7°C. The emulsion is coated upon gelatine-chrome alum substratumed glass.

For general details of the operations of emulsification, digestion, washing, coating, and drying, the following works should be consulted: Abney, Photography with Emulsions; Abney, Instruction in Photography, preferably 8th, 9th, or 10th editions; Eder, Handbuch der Photographie.

For the machinery employed in the manufacture of dry plates, *see* A. J. Munro, Photo. Journal, 1920, lx. 209.

The Photographic Dry Plate as a Recording Surface.

The production of a permanent record of the optical image formed on the focussing screen of the camera depends upon the change brought about by the action of light in the layer of sensitive material of the photographic plate, which change is completed by the operation of development, and this record constitutes the photographic negative.

The practical requirements of negative making demand an assemblage of minute sensitive particles uniformly distributed in sufficient

quantity. Inasmuch as the substance employed, the silver halide or halides, have not enough natural cohesion to ensure mechanical stability and constancy of arrangement, the particles must be suspended in a medium, and if the medium has not enough stability of its own to meet these requirements, a support must be provided. Under the conditions which obtain we have a film of the medium of reasonably uniform thickness resting on glass or celluloid, and in this film there is diffused particles of the sensitive halide complex. The media used are pyroxylene and gelatine. It is quite easy to consider the medium as merely a mechanical agent,[1] but it so happens that neither of these bodies play such a modest part. It is perfectly well known that the pyroxylene used in the collodion processes has a very important influence upon the character of the sensitive silver salt formed in its presence and in its subsequent behaviour, and this is even more marked in the case of gelatine.

The sensitive film of the photographic dry plate is not a homogeneous mass, but one of granular nature, the actual sensitive material consisting of 'grains' diffused through a layer of gelatine, and these 'grains' differ amongst themselves both in their form and size, in their sensitiveness to light, and in their amenability to subsequent development. To account for some of the properties of the gelatine film, Quincke has assumed the gelatine to possess a sponge-like character—a system of cells filled with liquid, the cell walls being of greater concentration of the colloid than the weaker solution which fills the cells. In these cells there exists the sensitive particles of halide which may be crystalline or may be a complex of the crystalline salt with gelatine and water (*see* Mees, The Physics of the Photographic Process, J. Franklin Inst. 1914; also The Structure of the Photographic Image, *ibid.* 1921, cxci. 631; and W. D. Bancroft, The Photographic Plate, J. Phys. Chem. 1910, xiv. 650). The size of the grains varies between ·1–3μ, according to the emulsion, and the thickness of the film between 10–12μ.

The quality of glass used for commercial dry plates and the method adopted in the dry plate factory do not permit of perfectly uniform emulsion films being produced, and in the case of celluloid the problem is still more difficult, nevertheless the coating is sufficiently uniform to meet the necessities of the purpose for which the majority of sensitive plates and films are made. It is only for special purposes where investigation on certain properties of the dry plate are to be made that greater uniformity is necessary. When the coating of emulsion is applied to the plate the mass is caused to set quickly, and this ensures, in so far as is practicable, reasonable uniformity in the distribution of the sensitive complex. If the drying be properly conducted there results a film, the exterior surface of which is smooth, but there are differences in this respect according to the emulsion. Any appreciable departure from smoothness—which after all is in this respect purely a relative term—will mean an increase in the 'scatter' at the surface and tend to produce deterioration of a critical image. The film may exhibit internal strain, more particularly near the edges (*see* Frank E. Ross, Image Contraction and Distortion on Photographic Plates, Astrophys. J. 1920, lii. 98). The physical condition of the film at the moment of exposure, and the subsequent operations by means of which the exposed photographic image is converted into a completed visible record, affect the accuracy of that image and its identity with the optical image by which it was produced. Certain of the defects from which negative images suffer may be eliminated by good procedure and manipulation, but there remain many which can only be mitigated, and their avoidance will only take place with improvement in the sensitive film. Many of the deficiencies are only of moment where critical work is concerned, as in astronomical photography, photo-micrography, and photo-spectroscopy, and although for the more ordinary everyday applications of the craft in which the sensitive surface finds employment, any improvement desirable for the processes designated will when made be of general service.

Halation.—Amongst the chief influences of a harmful character are halation, granularity of the image, and imperfect resolution. By 'halation' (photographic irradiation) is meant an extension of the image beyond the confines set by the original optical image. This defect is referred to by Abney in popular language as a 'blurring' of the image, for instance, the encroachment of the high lights on a darker portion next to it (Instruction in Photography, 1905, 11th ed., 57), or in more general terms by Chapman Jones, 'The word in its broadest sense indicates the spreading of light beyond its proper boundaries in the image' (Science and Practice of Photography, 1904, 4th ed., 367).

The subject was considered by Abney mathematically in 1875 (Phil. Mag. 1875), and in its application to practical work more directly before the Photographic Society of Great Britain in 1881 (Photo. Journal, 1881), by Eder (Handbuch der Photographie, ii. 90, and iii. 103), and by Drecker (Zeitsch. fur Wiss. Photo. i.), and by many others.

The causes leading to the defect are:—

(*a*) Scatter of light at the surface of the plate. This may occur in a dry plate if the surface be not perfectly smooth, but the trouble from this cause is only very slight in the great majority of instances. It arises principally in wet collodion plates, owing to the film of liquid upon the surface, and was found in dry collodion plates by the bath method when such were in vogue, and sometimes when a particular 'preservative' was employed (*see ante*).

(*b*) Scatter of light by the sensitive particles in the film which leads to a lateral extension of the image, so that the image of, for example, a point source becomes a fuzzy disc which increases in size with increase in the exposure, the actual extension differing, other things being equal, with the particular plate. In a series of exposures to such a source—presuming the brightness to remain constant—the increase in size of the developed image will be proportional to the logarithm of the exposure time, such increase being a measure of the 'scatter' or turbidity of the plate. Scatter halation shows in the image on paper (bromide papers), and has

[1] Colloidal silicic acid plays the part of an inert medium for silver bromide (*see ante*).

been detected even in the thin film of a daguerreotype. This form of halation is frequently termed *irradiation*, but sometimes this word is applied to all the causes leading to image extension, which is confusing.

(*c*) The light not absorbed by the film reaches the two surfaces of the support, and a portion of the bundle of rays suffering reflection reaches the under side of the film where action takes place, the effect showing on development as a separate zone around the image. Assuming the point image as in (*b*) the developed image will be surrounded by a ring, the diameter of which will increase as the thickness of the support becomes greater. The distance of the maximum is directly proportional to the thickness of the support, and the intensity proportional to the square of this thickness. The ring distance depends also upon the wave-length of the incident pencil, being less for light of shorter wave-length (Scheffer). With more prolonged exposure the density of the primary ring increases, and with further exposure a second ring appears, and so on. At the same time the point image becomes extended by lateral scatter, and in a series of prolonged exposures will be found to have reached the primary ring. With thin supports, as in celluloid-coated surfaces, this form of halation is sometimes assumed not to exist, but this is not quite correct. Considering again the image of the point source the ring with a thin support will be of small diameter, but is often strong, but so near to the central point that it appears to be part of it, actually presenting a similar appearance to that produced in an image laterally enlarged by 'scatter.' Nevertheless in practice considerable improvement obtains by the use of thin-coated celluloid film, and these with a large number of subjects may be said to yield 'reflection halation' free negatives provided that undue exposure be not given.

Scheffer, in an admirable account of halation (On the different forms of Halation, 5th Int. Congress Photography, 1910, *see* Brit. J. Photo. 1910, lvii. 683), designates the forms *b* and *c* as D halation and R halation respectively, and refers also to incidental causes of the defect as those due to the lens and to reflection from the inside of the dark slide. The latter, however, is scarcely germane to the subject, for it is merely one of the causes of 'fog' which is independent of the state of the sensitive surface, and is almost negligible in properly made slides. It would seem better to limit the use of the term rather than extend it unduly. Renwick (What is Halation? Brit. J. Photo. 1911, lvii. 894), like Scheffer, includes extension of the image due to faults in the lens, as lack of perfect transparency in the optical glass, and, what is tantamount, to deposit on free surfaces, reflections from surfaces of the elements in the components, and, as to influence on the *form* of the defect in particular instances, to the iris diaphragm. The defects from these causes he designates 'spurious halation.' Considerable influence in negative making is assigned to these, which is quite in accord with daily experience with the camera. To the reflection from the support—the R halation of Scheffer—Renwick would apply the term *halation*, reserving for the scatter effect—the D halation of Scheffer—the word *irradiation*, a classification which makes for clearness.

With respect to avoidance of the different forms of the defect, it may be observed that with suitable plates and carefully judged exposure the (*b*) defect *irradiation* is not of great moment in ordinary types of work where the image consists of relatively broad areas (continuous tone negatives—landscapes, architecture portraits), but in fine element images with sharp transition (broken-tone), as in negatives of fine line drawings, ruled screen negatives—dot images—the defect may be serious, more especially when care is not taken to ensure 'correct' exposure. It is also a considerable detriment in astronomical photography and in photo-microscopy, and particularly in negative making of line spectra, especially when the negative is of spectra containing lines of widely different orders of brightness. The amount of 'scatter' varies with the emulsion, and it is not necessarily least where the grain is the smallest (*see* Mees, Proc. Roy. Soc. lxxxiii. A, 559). The scatter is a combination of reflection 'scatter' and diffraction, and in very fine grain films the latter may predominate, in coarser grain layers the reflection may be sufficient to obliterate the phenomena due to diffraction. The reflection will be independent of wave-length, but not so the diffraction, so the amount of scatter will differ with light of different frequency. The total scatter of a particular film may be determined by measuring the rate of growth of the diameter of fine line image with increase in exposure, which yields a figure of value termed the *Turbidity Constant K*. The scatter effect may be to some extent reduced by staining the film (Waterhouse, Eder, Scheffer) with a yellow inert colour compound, but to produce any appreciable result the stain must be considerable, and this necessitates increased exposure. Scatter, as stated, increases with exposure, and in practical negative making disregard is often shown in judging exposure, with the result that certain defects produced—as the increase in line breadth in copying of line drawings—are taken to be inherent when they only result from unsuitable material and careless manipulation. The production of a well-defined image is not alone a question of fine grain—as assumed by many practical photographers—'the reason that fine-grained emulsions give images sharper in outline than those of coarser grain being that fine-grained emulsions usually have high contrast (γ) and a low turbidity, so that they give good sharpness of an edge apart from all questions of grain. If materials are used, however, which have high turbidity and low contrast, they will not give sharp-edged images, even though the grain size may be small' (Mees, Structure of the Photographic Image, Research Laboratory, Eastman Kodak, No. 109, 1921). In the paper quoted 'sharpness' is expressed as equal to γ/κ.

The subject of 'scatter' or 'irradiation' in relation to the photographic image, notably with respect to the important question of 'resolving power' of a sensitive emulsion film, has received considerable attention, and in addition to the communications already cited reference should be made to the following papers: Mees, On the Resolving Power of Photographic Plates, Proc. Roy. Soc. 1909; W. Scheffer, ditto, Brit. J. Photo. 1910, lvii. 24, 453, 576; Mees,

On Irradiation and the Resolving Power of Photographic Plates, 5th Int. Congress Photography, 1910, Report, 156–166; W. Scheffer, On the Resolving Power of Photographic Plates, *ibid.* 384–386; E. Goldberg, On the Resolving Power of the Photographic Plate, Photo. Journal, 1912, lii. 300–319.

The extension due to 'c,' viz. that due to reflection from the back of the support—the true 'halation' according to Renwick's nomenclature—can be avoided by placing in optical contact with the back surface of the support an absorbing medium of the same refractive index as the glass. This condition would be difficult to fulfil accurately, but in practice a sufficiently good approach may be made by a varnish of bitumen, a suitably stained collodion, or a paint of pigment with gum and caramel in aqueous alcohol, which diluent permits rapid drying. 'Lamp-black' is used preferably to any other pigment. The caramel should be the so-called 'spirit soluble' product. Many materials for 'backing' are employed by dry-plate makers, and as a general rule they are reasonably effective for the purpose, the aim being to produce a medium which will readily dissolve away in the solution used for development, a convenience appreciated by users. The medium employed must not exercise any detrimental influence during development. Certain backings have been found to lead to 'desensitising' (*q.v.*) which may be an advantage. Since this fact was observed it has been proposed to introduce into backing media bodies which are known to be 'desensitisers.' Other methods of preventiug reflective halation have been employed, as in the case of the duplex-coated plates of Sandell, where the under layer was of an emulsion of lower speed than the upper. In practice these plates were found to give an improvement in the negatives as against single-coated film then generally used, but the inconvenience due to the thick film, in fixation, washing, and drying, contributed to the causes which led the method to be abandoned, but it has since been revived for negative plates (Kodak).[1] A dyed gelatine layer has been suggested (Magerstadt), and Luppo Cramer has investigated the use of under-coatings of mercuric iodide and copper ferrocyanide in gelatine, but these are not inert towards the halide emulsion. Oakley employed a gelatine under-coating containing hydrated oxide of manganese produced by treatment of a gelatine substratumed plate with potassium permanganate (Photo. Rundschau. 1896, 320), and this principle and the particular agent has been employed with success in commercial dry-plate making. On fixation in a solution of sodium thiosulphate containing sodium bisulphite the oxide in the under layer is decomposed and the products washed out, leaving the film colourless. The plates prepared with this form of under-coating, so far as avoiding halation is concerned, are satisfactory.

[1] The principle of duplex coating has recently been applied for another purpose, viz. for making positives. The 'slow' under-coating is not employed in the making of the primary image, for the exposure is such that the more sensitive upper-coating only is influenced. After development a second exposure is made, and the upper coating removed when the under-coating is developed and yields a positive image (J. Soc. Chem. Ind. 1919, 513 *a*).

Inasmuch as the maximum influence of this form of halation occurs during exposure in the under side of the film—that in contact with the support—it would appear that the developed effect would be variable according to the mode of development, and this has been found to be true in practice for cases where the exposure has not been unduly prolonged. By means of a concentrated developer the effect can be to a certain degree confined to the upper layers of the film, and such a procedure produces a less halation effect in the developed image than is the case with a more dilute developer acting for a longer period (Renwick). One of the most noticeable effects produced by 'backing' is the improvement in the gradation in the high lights of negatives, which shows in a marked manner in portraiture when white or very light draperies are portrayed, even where the exposure of the plate has not been undue. In consequence backed plates or films for these and photographically similar subjects are advantageous. It is entirely an error in practical negative making to assume that 'backing' is only advantageous when the subjects present strong contrasts.

Since the opacity of the emulsion film to light increases as the frequency of the light increases, and 'halation' arises from the light *transmitted* by the film, it follows that there will be a difference in the amount of halation according to the wave-length of the incident light. In consequence, although the colours reflected from objects are mixed colours, the tendency will be when the plate is of the panchromatic type to show differences in the amount of 'halation' with objects of different colours of the same brightness. With 'ordinary' plates, however, this condition would not hold in view of the different spectral sensitiveness, the light of relatively great wave-length when transmitted and reflected not acting. When a source of light such as the mercury vapour lamp is used (where the photographically effective light is of short wave-length) and well coated 'ordinary' plate is employed the best conditions obtain for the avoidance of halation, so far as the plate and illumination of the subject can influence the result.

Grain in images.—An important characteristic of developed images is that of graininess or coarseness, which shows frequently to an unpleasant extent in images after enlargement. By *graininess* is meant something different to 'grain,' which has a precise meaning where employed by the photographic chemist, who uses the term to indicate the original particle of the sensitive salt, or the particle in the developed image. Absence of graininess means the absence of visible texture, and its presence would arise from the aggregation of grains or to a segregation of aggregates, and the avoidance of these phenomena is greatly to be desired.[1] The subject has recently been most carefully investigated quantitatively by Jones and Deisch (Jones, D. Loyd and Deisch, Noel, Measurement of Graininess in Photographic

[1] An early paper on the subject of 'grain' in dry-plate negatives by R. J. Wallace (The Silver Grain in Photography, Yerkes Observatory, July, 1904) is of considerable interest as one of the earliest examples of careful consideration of the problem.

Deposits, J. Franklin. Inst. 1920, cxc., Reports Research Laboratory, Eastman Kodak, No. 99; *see* also Brit. J. Photo. 1920, lxvii. 689, 706). The authors postulate three states in the unhomogeneous image: (1) *graininess* due to the existence of individual particles of silver, (2) *graininess* due to clumping, and (3) *graininess* due to agglomeration of the clumps; and state that 'The graininess of a plate of given performance is dependent on the grain characteristics of the emulsion,' and that 'the avoidance of the defect is in many respects a problem for the plate maker.' The authors observe that 'previous investigations have shown that the size of the silver grain is almost independent of the composition of the reducer,' but that 'there is a very appreciable difference in the *graininess* produced by different developing agents.' Rapidity of development does not necessarily lead to a low graininess in the deposit, and although development proceeds more rapidly at a higher temperature, the graininess is not reduced at that condition. With *p*-phenylene diamine in solution with sodium sulphite—a developer originally introduced by Lumière and Seyewetz (Bull. Soc. France Photo. June, 1900 and 1904) for the production of fine grain images—low graininess is produced, but the plates require considerably extended exposure and the gamma (contrast) values are low. The addition of alkali increases the developing action but produces more graininess, and this effect is adduced by the present investigators to be due to a change in the type of development, viz. from 'physical' to 'chemical', with certain reservations.

Of 'chemical' as against 'physical' developers ferrous oxalate appears to be the best in respect of the avoidance of 'graininess,' but is closely matched by an ordinary amidol developer. With a quinol-sodium carbonate developer increasing the carbonate content even up to saturation gave a decrease in 'graininess.' With quinol-caustic soda there is a disintegrating action on the film owing to the caustic soda, compared with the most concentrated quinol-sodium carbonate developer tried, and the former developer showed more 'graininess' than the latter. With pyrogallol in relatively low concentration and sodium carbonate, 10P : 37·5A, gave less 'graininess' than a higher pyrogallol content with lower sodium carbonate value, 20P : 25A, though the two developers gave deposits which approached the same value of 'graininess' in the higher densities. With respect to potassium bromide—the restrainer—variations in this agent do not appear to produce much difference. Negatives developed for high gamma values show a more pronounced grain than negatives developed to a low gamma (contrast). The graininess in relation to density is constant for a particular batch of emulsion, and is approximately so for different batches of the same type emulsion, but shows great differences for emulsions made by different procedures.

Resolution.—The expression 'resolving power' of a sensitive surface is applied to its capacity for representing as separate images on the surface separations which exist in the optical image or an image by whatever means produced. Quantitatively, the figure of value representing this resolving power is the expression of the space between contiguous images that are just separated when developed or printed as in the case of print out sensitive surfaces. From the brief observations made here upon the photographic film—its want of perfect unhomogeniety and the consequent scattering of the incident light—it will be seen that the resolving power of such surfaces will vary, and in consequence, since resolution is important in many branches of photography, the determination of the extent to which a surface will resolve is a matter of moment. Resolving power is considered in relation to the capacity of the eye in this respect, and the fact that the image is composed of measurable particles, aggregates of these and further clumps of aggregates (Jones and Diesch, *see ante*) makes it necessary to consider the power as it exists in the surface *ab initio*, and not after the image produced on the surface has been amplified, for example, by enlarging.

Considerable attention has been paid by many observers to the quantitative determination of 'resolution,' notably by Scheffer, Mees, Goldberg, Lehmann, Nutting, Huse, Ross, Tugman, and on grain size as a part of the problem particularly by some of the investigators cited, by Bellach, and, in addition, for wet collodion surfaces, by Monpillard and by Frary and Woollet. The methods adopted for determining resolution have varied, but the most satisfactory appears to be that of Mees (Report 5th Int. Congress Photo. 1910, 156–171; *see* also Huse, K. J., Opt. Soc. Am. I. 1917, 119). Mees produced optical images of about 1 mm. long on the particular surface under very rigid conditions, of a converging transparent grating consisting of alternate opaque and clear sectors of about 1·5 of angle. The developed images were examined under the microscope for the purpose of ascertaining the distance from the apex at which the image was first resolved. From the known value of the spacing in the reduced image at any point a figure of value is found, the particular figure representing the number of lines to the millimetre resolvable. Another method is that of Tugman (O. Tugman, Resolving Power of Photographic Plates, Astrophy. J. 1915, xlii. 331), who places against the sensitive surface an accurately prepared knife edge the surface being then illuminated. In the developed image the density gradient at the edge of the image under the obstruction is measured. In either method the effect of heterogeneous and homogeneous light can be measured by adopting either as a source of illumination. The method measures the rate of spreading, and this can be done for different conditions, not only of illumination, as stated, but for any other condition that might be assumed to exercise an influence. The method of Mees has yielded valuable results, and it appears to be considered, in view of certain experimental difficulties in the later plan of Tugman, to be on the whole the more advantageous.

Resolution has been shown to rest upon the turbidity of the emulsion film and upon the contrast yielding function of the plate which determine the 'sharpness factor' (*see ante*). It also depends on the 'graininess' of the developed image (*see ante*). Since sharpness varies with

the frequency of the incident light, it follows that resolution is influenced by varying wavelength being greater as this factor becomes less. Thus upon ordinary slow plates, Huse (Photographic Resolving Power, J. Opt. Soc. Amer. 1917, i. 119; Reports Research Laboratory, Eastman Kodak, No. 61) found that the resolution to blue light was much 'higher' even than that given by exposure to 'white' light. With the orthochromatic plate the same was true, the resolving power to the blue light being higher. On the panchromatic material the resolution was the best in the blue, dropping in the green and rising again in the red, but not to as great a value as given by the blue light.

The same author has demonstrated that wide differences in resolving power result from the use of different reducing agents in the developer, and that the 'correct' exposure is important for the production of the highest value (*see* also F. E. Ross, Photographic Sharpness and Resolving Power, Astrophy. J. 1921, lxii. 201).

The following communications in addition to those given should be studied: M. Monpillard, Experiments on the Grain of Silver Images, Bull. Soc. Francais, 1907, *see* Brit. J. Photo. 1907, 936; Francis C. Frary and Guy H. Woollett, Micro-Structure of Wet Plate Negatives, 8th Int. Cong. App. Chem., *see* Brit. J. Photo. lx. 879–881; E. Lehmann, Resolving Power of Photographic Films and the Reproduction of Fine Detail, Zeits. J. Reproductiontechnik, 1912, *see* Brit. J. Photo. 1913, lx. 7, 23, 48. These papers have reference mainly to collodion films. The differences in the physical state of the images in collodion shown by different processes were well known to the early experimentalists and practical manipulators in the process (*see*, for example, Hardwick, Manual of Photographic Chemistry, 4th ed. London, 1857, 145).

Accuracy of rendering.—Upon a consideration of the value of the gelatine dry plate for the precise rendering of the optical image, Eder, after experiment, came to the conclusion that in so far as this might be affected by the expansion of the gelatine film the dried negative showed, when examined against the original, no expansion or contraction. He further investigated, whether or not any change occurred in the dimension of lines owing to electrolytic action during development, and as the result of his experiments, came to the conclusion that the dimensions of the image on the plate as compared with the original source suffered no alteration with short development using ferrous oxalate, and that practically the same result obtained with ten times the normal development time provided that no 'fog' supervened. It was found, however, that the result was not so good when 'fog' ensued, and it was pointed out that this was likely to occur with alkaline pyrogallol, when it was found that 'the edges of the lines were not quite sharp.' Eder concluded that for exact reproductions development should be as rapid as possible, and that it must not be allowed to continue after fog had made its appearance (Modern Dry Plates, Eng. ed. 1881, 80–89). These experiments were made in the early days of the dry plate, and do not appear to have been followed up, though numerous observations on image accuracy of a more or less general nature are to be found scattered in photographic literature. The phenomena occurring in Eder's experience, in so far as the second part of the statement is concerned, are dealt with fully in the investigations upon 'sharpness' and 'resolution.' Some of the many influences militating against accuracy in photographic images have recently been carefully investigated by Ross (F. E. Ross, Contraction of Photographic Images, Opt. Soc. America, Dec. 27, 1918); Reports Research Laboratory, Eastman Kodak, No. 76; Image Contraction and Distortion on Photographic Plates, Astropyhs. J. 1920, lii. 98; Reports, *ibid.* No. 94), with particular reference to astronomical photography where any error is of considerable moment. It was found that errors such as the displacement of stellar discs were possible owing to the original faulty drying of the emulsion film in the factory, but that by re-wetting and properly drying these errors may disappear. With certain developers, viz. those which have an insolubilising action upon gelatine owing to the association of the latter with the products of oxidation, such as alkaline pyrogallol or quinol, distortions also occur which depend upon the image, its size and shape, and upon the degree to which development has been carried. With a series of minute images, as in a star cluster, for example, one will draw towards its neighbour. The author states that 'the cause is to be found in a smaller water content of the tanned gelatine within and in the immediate neighbourhood of the image. The image, in consequence, dries more quickly than the surrounding gelatine, stresses are set up which, being unbalanced, produce contraction of the image of the neighbouring gelatine' (Report No. 76). A study of this paper shows the errors that are likely to occur under particular conditions, and the results of the investigation are of moment in work where extreme accuracy is necessary, as in the instance cited and in photo-spectroscopy and photo-micrography.

Selective absorption of the image material.—In the simple consideration of the negative as a regulator of the light which falls upon the sensitive surface employed for positive production the image-forming deposits may be assumed with respect to hue to be of neutral character, and thus exercising no selective absorption, so that the spectral composition of the transmitted light is the same as the incident light. In consequence, the effect is due only to differences in intensity of the light transmitted, and the negative is merely a regulator in this respect. Given a series of transmissions it is immaterial how it is produced, so far as the effect in the sensitive surface used for positive making is concerned. In practice the condition is not so simple. Deposits produced upon wet collodion with plain iron development approach neutrality, although even here differences are noticeable. On certain fine grain plates with ferrous oxalate development reasonably neutral deposits can be obtained. All phenolic reducing agents which are employed in developing solutions—and these constitute the principal bodies used for the purpose—yield coloured oxidation products,and these, which are generally more or less insoluble in the solution, form complexes with the silver grain. If the silver image

be removed by any suitable agent which does not appreciably affect the stain, as, for example, cupric bromide followed by sodium thiosulphate, a colour image will remain, the gradations of which correspond, roughly, with those of the original silver deposit. This is the 'stain image,' and its character will depend in the main upon the plate and the developing agent used, in the concentration of sodium sulphite in the developer and the time of development. With high sulphite content the stain image is lessened but it is never eliminated. This stain image is not to be confused with a general stain due to a discoloured developer or faulty manipulation. The image material is, therefore, coloured and, in consequence, exercises a selective absorption, the amount of which will depend upon the conditions of production of the negative. The contrast in a negative is in practical photography judged by reference to the eye, the retina being the sensitive surface. When the negative is used for photographic printing the sensitive surface is one having a different spectral sensibility to the retina, one whose sensitiveness is, in general, far less extended. In consequence, the contrast in the positive is not identical with what might be anticipated by mere visual examination, for when the negative is judged, more particularly in ordinary artificial light, the observer does not always take into account sufficiently the part played by the coloured constituent of the image, indeed, stain variations are difficult to assess under this condition. The effective opacity to the source of light may, for a particular printing surface, be increased by the inclusion of the stain, and this is equivalent to an increase in silver density, only the latter is noticeable by whatever illumination the negative is examined, whilst the part which will be played by the stain is often not considered. The so-called 'printing quality' will vary according to the light used and the sensitive surface. For example, a silver printing paper which has its maxima of sensitiveness in the blue would yield greater contrast with a white light by the presence of the yellow stain image than would a bichromated gelatine tissue which has its maximum in the blue-green. It should not be assumed that this is necessarily a defect, for the production of 'stain image' may be controlled and may serve a useful purpose. In the development of aerial negatives during the recent War, the printing quality was largely determined by the regulated stain image (non-sulphited pyro-metol developer). The stain image should be, however, kept reasonably uniform in amount, otherwise judgment of printing value by preliminary visual examination becomes difficult, and, moreover, the relation of contrast to the printing medium employed is disturbed. This subject, in its fundamentals, has been considered by Jones and Wilsey (Spectral selectivity of photographic deposits, J. Frank. Inst. 1918), whose paper should be studied.

Spectral sensitiveness of the material.—The spectral sensitiveness of the ordinary type of the silver bromide gelatine plate extends from the ultra-violet 380$\mu\mu$ to the blue-green 490$\mu\mu$ with a maximum of 450–470$\mu\mu$. On prolonged exposure to the normal spectrum very little extension of the sensitive region is observed, but the density of the region of greatest activity increases on development.

The condition that the retinal sensitiveness differed from that of the photographic surfaces has been, since the earliest days of photography, a bar to truthful representation in monochrome of the visual picture, and it has only been within recent years that any real approximation to correct translation has been practicable. The original discovery of Vögel in 1873 (Ber. 1873, vi. 1302 ; *see* also Photo. News, 1873, xvii. 589), that the spectral sensitiveness of silver bromide in the photographic surface might be extended from a confined continuous zone in the ultra-violet and the blue by the addition of an isolated region in the yellow, through the presence in the emulsion film (collodio-bromide of silver) of the coal tar colour, *Red Corallin* (which was probably the rosolic acid salt of rosaniline), gave birth to the so-called orthochromatic plate. In 1875 a new class of colour compound was employed by Waterhouse (J. W. Waterhouse, Experiences with Red Sensitisers, Photo. Journal, 1904, xxviii. 165–171), who showed that *eosin* (*eosin yellow shade :* sodium salt of tetra-bromfluorescein) conferred sensitiveness on collodio-bromide plates for green and yellow. This compound was afterwards employed with gelatine plates under the patent of Clayton and Taillfer (1882) by the addition—with ammonia—to the emulsion or by bathing the finished plates in an ammoniacal aqueous alcoholic solution. Eosin sensitised plates were introduced commercially by Edwards in 1884. In this year Eder recommended the employment of *Erythrosine* (sodium salt of tetra-iodofluorescein) as the better colour compound of this class, and its use still persists. In 1886 Mallman and Scolik (Photographische Correspondenz, 1886) proposed an erythrosine silver compound in aqueous ammonia which gave valuable results. The band of sensitiveness for eosin does not extend to the D line, and the maximum lies in the green, whilst with erythrosine the sensitiveness extends beyond D. Becquerel in 1884 (Compt. rend. lxxix. 189) observed that *chlorophyll* behaved as a sensitiser to silver bromide and iodide, showing several maxima of effect in the red and yellow regions between B and C and C and E. This substance was used by Ives with considerable success alone, and later in conjunction with eosin in collodion emulsion (F. E. Ives, Philadelphia Photographer, Dec. 1879, 365, Chlorophyll ; and Brit. J. Photo. 1885, xxxii. 527, Chlorophyll and Eosin).

A considerable number of colour compounds were tried as sensitisers by the early investigators (Vögel, Eder, Waterhouse, Albert, and others), such as *Orange Coralline* (*Aurine*), *Naphthalene red*, *Fuchsine* (aniline red), *Aldehyde green*, *Methyl violet*, *Cyanine blue*, *Quinoline red* (cyanine red), *Alizarin blue*, *Rhodamine*, and many other bodies in related or unrelated classes, with more or less success, as well as certain vegetable natural colouring matters in addition to the chlorophyll cited. The sensitising properties of the colouring matter *Cyanin* (produced by the action of caustic alkalies on the reaction body obtained from amyl iodide and equimolecular proportions of quinoline and lepidine, Greville Williams, 1856, Chem. News, 1859, i. 15) caused considerable interest

from the time of its first employment by Vögel. This body conferred orange and orange-red sensitiveness upon silver bromide, but the plates so prepared showed spots and fog. This defect was to a certain extent overcome, although not entirely so, by the use of *Chlorcyanin*, which was suggested by Eder. The same investigator proposed the employment of erythrosine with cyanin, and this mixture is stated to have increased the red sensitiveness, but to have greatly depressed the general sensitiveness (Waterhouse). The depression of the speed of a plate by the addition of sensitisers has since been found to be general, though varying in degree. A notable sensitiser of this early period for gelatine plates was the ' Azaline ' of Vögel, which was a mixture of quinoline red and cyanin (quinoline blue). The quinoline red (prepared by the action of benzotrichloride on quinaldin and isoquinoline in presence of zinc chloride, Jacobson, 1882) sensitised for yellow-green and pure yellow, and the cyanin (quinoline blue) for orange and orange-red. The association of the quinoline red was found to overcome some of the photographic defects of the cyanin.

So far it would appear that the sensitisers employed had consisted of two classes, the one class bodies selected somewhat haphazardly, and the other class a group of compounds which were related to one parent, viz. Fluorescein, derivatives of which—Eosin, Erythrosine, Rose Bengal, Phloxine, Rhodamine—were selected, but in 1903 a departure was made which has led to fruitful results.

It had been shown by Hoogewerf and van Dorp (Rec. trav. chim. 1883, ii. 28, 41) and Spalteholz (Ber. 1883, xvi. 1847) that cyanin and its analogues are produced by condensation of one molecule of a quinolinium alkyliodide with one molecule of lepidinium alkyliodide. The same investigators independently found that a series of compounds could be formed by the condensation of equimolecular proportions of a quinolinium alkyliodide and quinaldinium alkyliodide. These are the '*iso*cyanins' (*see* Rec. trav. chim. 1884, iii. 344). Miethe and Traube recognised the possible value of these *iso*cyanins, and in 1903 showed (Chem. Ind. 1903, xxvi. (3) 54) that a member of this series (condensation product of ethyl quinolinium iodide with ethylquinaldinium iodide), which they named *Ethyl red*, conferred upon a gelatino bromide plate an additional sensitiveness, so that the ordinary region was extended into the orange, and that the plates were free from many of the defects found with the original cyanin. This striking advance was followed by König, who produced other compounds as *Orthochrom T.* (*p*-toluquinaldine-*p*-tolylquinoline-ethylcyanine), *Pinachrome* (*p*-ethoxyquinaldine-*p*-ethoxyquinoline-ethyl cyanine) and *Pinaverdol* (*p*-toluquinaldinequinolinemethyl cyanine). These colour compounds were introduced by Meister Lucius and Bruning as sensitisers (D. R. P. 167159 and 167770, 1903). As the result of further investigation by König, products resulting from the treatment of *quaternary* quinolinium and quinaldinium salts in the presence of formaldehyde with alkali were introduced by the above firm, of which the most important was *Pinacyanol*,[1] which proved to be a much more powerful sensitiser for red than had hitherto been made (D. R. P. 172118 and 175034, 1905). By the action of an alkali with an oxidising agent upon quinaldinium salts an additional group of compounds was produced of which an important member is *Dicyanin*[1] (M. L. and B.), which sensitises for the extreme red. This colour compound is useful for spectrum photography in the red and infra red, but otherwise is not of great value (*see* Mees and Wratten, Photo. Journal, 1908, xlviii. 25). A series of isocyanin sensitisers was introduced by F. Bayer & Co. (D. R. P. 158078, 170648, and 170049) under the names of *Perikol*, *Isokol*, and *Homokol* respectively, of which *Homokol* proved to be a good sensitiser for green and what has, in particular, proved to be a ' difficult ' region, viz. the blue-green.

The special demands in the Services for the purpose of photography from the air during the War led to particular and sustained attention being paid to the subject of the *iso*cyanin bodies by Pope and Mills in the laboratories of the University of Cambridge with valuable results. Colour compounds were prepared which showed an advance on those hitherto produced, with the result that the production of panchromatic photographic surfaces has been greatly improved. Out of the number of bodies made under these investigations there was rendered available certain compounds with special properties suitable for the sensitising of silver halides, and these were named *Sensitol green* (synonymous with Pinaverdol), *Sensitol red* (synonymous with Pinacyanol) and *Sensitol violet*. These sensitisers are prepared in the University laboratories for general use. The original papers should be consulted with respect to the preparation, constitution, and sensitising influence of the many compounds prepared (Studies in Photographic Sensitisers, Part I., *see* Photo. Journal, 1920, lx. 183–198, and Part II., *ibid.* 1920, lx, 253–266; *see* also The Cyanin Dyes, W. H. Mills, Chem. Soc. Trans. 1920, cxvii. 579, 1035, 1550; cxxi. 455–466; and F. M. Hamer, *ibid.* 1921, cxix. T. 1432; and J. Soc. Chem. Ind. 1921, 791 *a*; Photo. Journal, 1922, lxii. 8).

Investigations upon the *iso*cyanin compounds have been conducted in other laboratories, and the following papers should be consulted: Laboratory Preparation of the Colour Sensitising Dyes, Pinaverdol and Pinacyanol, Colour Laboratory, U.S.A. Bureau of Chemistry, Brit. J. Photo. Col. Supp. 1919, lxvi. 34; H. Barbier, Bull. Soc. Chem. 1920, 427; J. Soc. Chem. Ind. 1920, 528 *a*; W. König and O. Treichel, J. pr. Chem. 1921, cii. 63; J. Chem. Soc. 1921, Abs. cxx. 738; S. Palkin and M. Harris, Preparation of Alpha, Gamma Dimethyl Quinolines, I., Bureau of Chemistry, U.S.A., J. Ind. Eng. Chem. 1922, xiv. 704.

Bloch and Renwick have shown (Auramine as a Sensitiser, Photo. Journal, 1920, lx. 145) that the basic dye *Auramine* (imidotetramethyldiamidodiphenylmethane) when used

[1] It should be noted that König did not consider the compound pinacyanol to be a true *iso*cyanin differing in this respect from a later introduction, *Pinacyanol-blue*, produced by Staehlin working under König at the Höchst Works (*see* Photo. Rundschau (1914), also Brit. J. Photo. 1914 lxxxviii., Col. Supp. 13).

[1] Commercial dicyanin is derived from 2 : 4 : 6-trimethyl quinoline.

alone upon silver bromide dry plates does not produce any sensitising effect, but that when employed in conjunction with an *iso*cyanin colour compound it enhances the sensitiveness which these bodies confer, although the auramine alone has no influence on sensitiveness; it further prevents the fogging tendency when certain particular *iso*cyanin compounds are used and prolongs the keeping qualities of the plates. If used with gelatino-silver chloride plates the auramine acts as a powerful sensitiser.

A new basic yellow colouring matter was produced by König and introduced (M. L. and B.) in 1921 under the name of *Pinaflavol*. This body—which is soluble in water—is stated to confer considerable sensitiveness on silver bromide plates for green and yellow practically without the 'gap,' which is shown when plates are sensitised with erythrosine (*see* Eder, Photo-Correspondenz, 1921, lviii. 29–31; and also Brit. J. Photo. Col. Sup. 1921, lxviii. 16). In the Eastman Kodak Research Laboratory new sensitisers for the far red have been made, of which the most prominent are *Naphthocyanole* and *Kryptocyanine*. Naphthocyanole is a homologue of pinacyanol, and is prepared by the condensation of betanaphthaquinaldine ethiodide with quinoline ethiodide in the presence of formaldehyde with alcoholic potash. This body sensitises with a strong maximum at 690$\mu\mu$ with a minimum in the green. Kryptocyanine is made by the condensation of lepidine ethiodide after the manner of Adams and Haller (J. Amer. Chem. Soc. 1920, xlii. 2661). In very dilute solution it sensitises on bathing for the extreme red. The maximum is at 760$\mu\mu$, but there is no green sensitiveness. This sensitiser is stated to be the best known for the near infra-red, but is inferior to dicyanin for the far infra-red (*see* Mees and Gutekunst, Report No. 147, Eastman Kodak Research Laboratory; and Brit. J. Photo. 1922, lxix. 474–475).

A new green sensitiser, 2-*p*-dimethylaminostyrlpyridene methiodide—produced by condensation by boiling of *p*-dimethylaminobenzaldehyde with α-picoline and piperidine in alcohol—has been prepared by Pope and Mills (J. Chem. Soc. 1922, cxxi. 946–947), which is stated to be the most powerful yet made for gelatino-bromide plates, showing almost uniform sensitising effect from the blue to about 560$\mu\mu$ with a fall to about 620$\mu\mu$. Other sensitisers may be made by replacing α-picoline by its derivatives.

The mode of application of the colour compound is by addition of a solution to the emulsion before coating or by bathing the plate at ordinary temperature for 3–4 minutes in an aqueous solution with the addition of ethyl alcohol (or sometimes methyl alcohol), and in certain cases with alcohol and ammonia, followed by washing in water, and, in some instances, with a preliminary brief washing in alcohol, before washing in water, after which the plates are dried rapidly in a current of air in a properly constructed drying box. The concentration of colour compound differs with the compound. In the case of erythrosine the concentration may be 0·5 to 1 : 5000, but for the iso-cyanin compounds 1 to 2 : 100,000 suffices. The colour will dye the halide and will be removed from the gelatine of the film on washing.

It may be observed that all dry plates will not prove suitable for the sensitising treatment. A plate must be chosen which will work free from 'fog' and should preferably have a low gamma value for blue-violet light, failing which there is difficulty in obtaining uniform action through the spectrum owing to excessive density in the blue-violet region (Wallace). The tendency with eosin sensitisers is to curtail any slight tendency to fog. The sensitised plates when properly prepared will retain their colour sensitiveness in good condition for several months if carefully stored in a clean dry atmosphere. In many instances combinations of colour compounds may be and are employed. Thus: *Pinacyanol* and *Pinaverdol* or *Sensitol red* and *Sensitol green*. *Pinachrome violet* may be employed with either *Orthochrome T.*, *Pinaverdol*, or *Pinachrome*, whilst *Sensitol green* can be used with *Sensitol violet*. *Pinacyanol* should not be employed with *Orthochrome T.*, *Pinachrome*, or *Ethyl red* (König).

The sensitising effect produced by using different colour compounds, and the most suitable conditions for their application, have been examined quantitatively by several investigators, and the original papers should be consulted: Sheppard and Mees, Photo. Journal, 1906, xlvi. 110–130, and Theory of the Photographic Process, London, 1907, 308; R. J. Wallace, Studies in Sensitometry, Astrophy. J. 1907, xxv. No. 2; 1907, xxvi. No. 5; F. Wentzel, Experiments in Colour Sensitising Chloride Emulsions, Brit. J. Photo. 1909, lxvi. i. to iv. 5, 22, 41, 64; G. Daur, Mixtures of Dyes as Sensitisers of Gelatine Plates, Brit. J. Photo. 1909, lxvi. i. to v. 572, 592, 610, 630, 649; F. M. Walters, jun., and R. Davis, Studies in Colour Sensitive Photographic Plates and Methods of Sensitising by Bathing, U.S.A. Bureau of Standards Sci. Papers, 1921, xvii. No. 422, 353–375.

The extension of the sensitiveness of the normal halide is not alone conferred by treatment with organic colour compounds. J. G. Capstaff and E. R. Bullock have shown (Production of Panchromatic Sensitiveness without Dyes, J. Franklin Inst. 1920, cxc. 871; Brit. J. Photo. 1920, lxvii. 710) that treatment of the silver bromide or bromo-iodide plates with a dilute solution of sodium bisulphite (2 p.c.) followed by water washing give increased colour sensitiveness, and that the effect was maintained —but the general sensitiveness enhanced—by following the treatment with a brief washing in a N/10 solution of sodium carbonate, or better, with a 0·2 p.c. solution of pure potassium bicarbonate neutral to litmus and free from chlorides. Extremely small amounts of soluble bromide and chloride inhibit the effect when present in the washing water, but have no such influence if they occur in the sodium bisulphite solution. The investigators do not offer any explanation which they consider satisfactory, but state tentatively that the effect may result from a partial reduction of the halide to metallic silver in colloidal condition, and such a nucleus has been shown by Luppo Cramer to act as an 'optical' sensitiser (Photographische Correspondenz, 1911, 184). Renwick (Action of soluble Iodides on Photographic Plates, Photo. Journal, 1921, lxi. 12, read Nov. 16th,

1920) has, in addition, demonstrated the sensitising action for orange and orange-red of dilute solutions of soluble alkali halide, and similarly, of alkali cyanides. Renwick, considering these phenomena, suggests an alternative view (Cor. Brit. J. Photo. Dec. 3rd, 1920, lxvii. 743). Having advanced the suggestion (Photographic Images, Visible and Invisible, Hurter Memorial Lecture, J. Soc. Chem. Ind. T. 1920 ; Brit. J. Photo. 1920, lxvii. 447, 463) that the ripened silver bromide grains in a gelatine dry plate contain colloidal silver in solid solution, and as the colour of the colloidal silver depends upon the state of aggregation—and that this is easily modified by traces of various salts—that as a result of the action of the alkali halide, cyanide or bisulphite, a change in size from a yellow to a greyer or bluer modification takes place and that this accounts for the observed effect (*see* R. Bruce Archey, Red Sensitiveness of Silver Iodide, Photo. Journal, 1921, lxi. 235, who confirms Renwick's experience). Sheppard (Photo. Journal, 1922, lxii. 88) considers that the effect is due to an orienating effect of iodide on the colloid silver formed by exposure itself, but that it does not take place with every kind of plate.

Correction filter.—For correcting the relatively excessive action of the more refrangible end of the spectrum a yellow correction filter is necessary. For this purpose an absorbing transparent screen, generally of a film of gelatine containing colouring matter —although the film alone is often used— optically sealed between parallel planes of glass so that no disturbance of the image takes place—is necessary. Very few yellow colour compounds available were quite satisfactory, until 1906, when Meister Lucius and Bruning introduced a compound to which was applied the designation *Filter yellow K.* This body is soluble in water, is stable in gelatine, absorbs ultra-violet strongly—save for a band of transmission at 300$\mu\mu$—and shows a gradual absorption in the blue; its defect, however, is that when used for low concentration filters the absorption in the blue is not sufficiently abrupt. It does, however, furnish for most purposes, in suitable concentration, filters that are satisfactory. During the War, when a supply of this colour compound was no longer available, a compound having similar properties prepared in the laboratories of the University of Cambridge was made available, and was designated *Filter yellow A.* (Ilford Co.).

In 1919 a new colour body was introduced from the Research Laboratories of the Eastman Kodak Co. (Brit. J. Photo. 1919, lxvi. 48 ; J. Ind. Eng. Chem. 1919, xi. 454). This compound is the sodium salt of glucose-phenyl osazone-*p*-carboxylic acid which was named *Eastman yellow.* The colour has nearly as strong absorption in the ultra-violet as *Filter yellow K.*, and a sharper absorption in the blue than that compound. It is, however, not so stable to light as *Filter yellow K.*, but is found to be sufficiently so for all practical purposes. For correction filters, *see* Mees, Dict. App. Physics, iv. 176–179.

Self-screened or non-screen colour-sensitive plates.—To avoid the complication entailed by the use of the correction filter in practice, and to secure other advantages, the method has arisen of combining in the film with the colour sensitiser a yellow colour compound. The idea of using a yellow colouring matter in the film appears to have been originally proposed for the prevention of ' irradiation ' (*q.v.*) (Eder, Vogel, Waterhouse), and later to correct for the excessive action of the blue. The first definite use in an emulsion film was probably by E. Albert. Jonas, instigated by Eder, investigated the possibilities of the method, and, as the result, published the details of a process for using ammonium picrate in conjunction with an ammoniacal solution of an erythrosine silver compound for sensitising and screening collodion emulsion (*see* Photo. Correspondenz, July, 1891 ; also Brit. J. Photo. 1892, xxxix. 168, 182), and eventually a yellow screening dye was employed in gelatine plates, particularly with erythrosine. For sensitising by bathing, *filter yellow K.* is effective in conjunction with *erythrosine*, and such a plate is satisfactory where yellow and green sensitiveness is required. For green, yellow, orange, and light red, *pinachrome* and *filter yellow K.* should be used, whilst for greater red sensitiveness *pinacyanol* should replace the *pinachrome.* It appears that all plates are not suitable for use with erythrosine, but this restriction does not apply to the other colour compounds (*see* E. König, Process Year Book, Penrose, London, 1909–1910; and Brit. J. Photo. 1910, lxvii. Col. Sup. 3.) Several types of these plates are now made commercially. The theoretical and practical considerations involved in their use have been discussed by Luppo Cramer (Photo. Rundschau, 1920, lxvii. 129). This writer points out that, with these plates it is possible by differences in exposure and development, to reverse the effects of the blue and yellow, and that for securing the best possible results an effective anti-halation ' backing ' is quite necessary. It may be observed that, with care, these plates are a valuable aid in negative making. The ' self-screening ' colour body reduces speed as against the same emulsion unscreened—and non-colour sensitised—as might be expected.

Influence of wave length in gradation.—The effect of the different frequencies of the incident light upon the gradation produced was considered by Chapman Jones (Photo. Journal 1900, xxiv. (new series), 279–286), who came to the following conclusions:—

(*a*) 'That gradation is not constant with varying wave length; (*b*) that the longer the wave length the steeper the gradation, except that it becomes less steep in the higher densities (the tendency to reversal being greater the longer the wave length), and also probably less steep in the lowest densities. The tendency apparently is to change in the opacity logarithm (or "density") curve in the direction shown in Fig. 9, by the difference between the curve marked "shorter wave length" [1] and that marked "longer wave length"; (*c*) that the differences in gradation are not due to different compounds in the film when specially sensitised, because they are shown in ordinary plates, and an increase in the difference of wave length gives an increase in the difference of gradation,

[1] (Note by present author. The curves should be consulted in the original paper.)

irrespective of the sensitising of the plate; (*d*) that the use of pyrogallol and ammonia leads to irregularity in this matter as in others, making the curve produced by the light of longer wave length less steep than it otherwise would be (or that of shorter wave length more steep). It seems probable that it is the ammonia that leads to this irregularity.'

Abney obtained results which agreed closely with those of Chapman Jones, but observed 'that the gradation is least steep at the region of maximum photographic effect, and increases in steepness on both sides of the region' (Proc. Roy. Soc. 1901, 68, 300).

Sheppard and Mees, considering (Investigations on the Theory of the Photographic Process, 298–307) these results, observe that in neither of the investigations were precautions taken to ensure that the photographic intensity of the light source remained constant for different hues, which fact would in itself produce different 'steepness of gradation.' They remark that great difficulty arises in the interpretation to be applied to the term 'gradation,' and proceed to a consideration of the question mathematically, employing the equation of Hurter and Driffield (Photo. Chem. Investigations, J. Soc. Chem. Ind. ix. 1890) for the effect of light upon a plate.

The equation of Hurter and Driffield referred to above is:—

$$D=\gamma \log \left\{p-(p-1)\beta^{\frac{E}{i}}\right\}$$

where $\log_\epsilon \beta=-\frac{1}{p}$, and p=the optical opacity of the unexposed surface, whilst D is the mass of silver which has been made reducible. γ is a development factor. Let us now write D′ for $\log \left\{p-(p-1)\beta^{\frac{E}{i}}\right\}$, so that $D=\gamma D'$. According to Sheppard and Mees, the term 'gradation' is sometimes used to mean γ, sometimes $\frac{dD'}{d \log E}$, and sometimes $\frac{dD}{d \log E}$, or what is the same thing $\gamma \frac{dD'}{d \log E}$, and from their experiments they came to the conclusion that alteration in wave length affects $\frac{dD'}{d \log E}$, but not γ; *i.e.* γ is not only constant for different exposures when the wave length remains constant, but γ remains constant when the wave length also varies, in other words, the alteration in $\frac{dD}{d \log E}$ may be fully explained by variations in the value of p for light of different colours.

The original paper should be consulted for the full development of the mathematical considerations and for the very interesting experimental methods adopted. Considering the work of Precht and Stenger (Zeit. wiss. Phot. iii.), and of the *iso*cyanine colour stuffs later used in sensitising, the authors observe that their work requires confirmation, but that the main conclusions are probably accurate (*see* also E. Lohmeyer, Zeits. f. Reproductionstechnik, 1908). A. Hnatek has shown (Zeits. wiss. Photo. 1916, xv. 271; J. Soc. Chem. Ind. 1920, 45 *a*) that when the densities of a negative are plotted against wave-length the curves show an $\int$ formation rising from the more refrangible end to a maximum (for ordinary plates) at about 450$\mu\mu$, falling to a minimum and rising again in the neighbourhood of 490$\mu\mu$. Orthochromatic plates show some differences in the region and in the value of the maxima. These several investigations show *some* of the difficulties which *at present* lie in the path of a purely photographic process for three- and four-colour process work, indeed, any process which depends upon colour selection by colour screens and unaided photography. In such processes—putting aside other limitations and all questions of incorrect procedure—a considerable amount of hand modification upon colour negatives and plates is still required.

In connection with this aspect of the action of light upon an emulsion film an interesting paper by Ross should be studied (Photographic Photometry and the Purkinje Effect, Astrophys. J. 1920, lii. 86). In this paper the investigator considers the effect of light of different wave-lengths upon the value of 'gamma' or contrast function in relation to the determination of stellar magnitudes, but the truths enunciated have a more general application.

Quantity of silver salt.—With respect to the quantity of silver salt for a given area of dry plate, it should be observed that the actual mass of the halide is not necessarily the criterion of value, for taking the density of image finally yielded as one important feature, this does not depend wholly upon mass, but on the physical condition of the salt. If for a given state a certain quantity be necessary, then with a smaller percentage a thicker coating is required, and this is a drawback in many respects in negative making. The quantity varies; Hurter and Driffield found in the earlier days of dry plate making between 26-49 p.c. of silver bromide. In a communication to the London and Provincial Photographic Association (unpublished) Haddon and Grundy gave the results of investigations on 22 English dry plates, and found the quantity of halides, bromide, or bromo iodide varied between 0·0955 to 0·2330 grams expressed as silver bromide per 100 sq. c.m. The authors stated that rapid plates contain on an average about 20 p.c. more silver than do the 'slower' or ordinary plates. In the case of a number of rapid commercial plates of British and Continental origin (10 examples) Tappen and Rekaschow (Photographische Correspondenz, Aug., 1908, xlv. No. 575, 362–364) found the amounts to vary on air dry plates between 0·425 to 0·627 gram of emulsion per 100 sq. cm., giving 41·44 to 43·44 p.c. silver bromide, the corresponding gelatine being 58·56 and 56·56 p.c. respectively. Assuming the percentage of the silver halide to be slightly over 42 p.c., and the average water content in the original emulsion, the authors came to the conclusion from the rapid plates examined that the average composition of the film might be stated as: silver bromide 38·5 p.c., gelatine 53 p.c., water 8·5 p.c.

According to Renwick, the dry plate to-day usually contains from 2 to 10 p.c. silver iodide in 'solid' solution in the silver bromide, *see* Photo. Journal, 1921, lxi. 12.

Influence of moisture.—An interesting instance of influence affecting speed of the emulsion film arises in the case of water, the presence of which during exposure lowers the value considerably. According to Sterry, 'a plate thoroughly wetted is decidedly slower than when it is dry' (Photo. Journal, 1895, xix. 121), and later, that 'a plate is invariably in its most rapid condition when thoroughly dried, the speed rapidly decreasing when moistened' (*ibid.* 1898, xxii. 269). E. H. Farmer came to the same conclusion (Brit. J. Photo. 1902, xlvii. 457), citing the presence of moisture in the film, which he found reduced speed, as one of the many influences of this agent. Similarly, K. Schaum (Eder's Jahrbuch der Photographie, 1903, xvii. 194) observed changes in the speed, which suggested an increase, as the mass of the film became drier. Sheppard and Mees studied the influence of water in the film, and observed that its presence at the time of exposure lowered the speed appreciably, but stated that 'the desensitising action of water is probably to be attributed to a slight amount of some foreign substance' (Investigations on the Theory of the Photographic Process, 1907, 257, 258, 262). A further contribution to this subject has been made by Cousin (Bull. Soc. Franc. 1919, 6, 27), but the question was only studied qualitatively.

The reciprocity law.—Abney in 1893 observed (Proc. Roy. Soc. 1893) that the sum of a series of brief exposures was not equivalent in its effect upon a sensitive photographic surface to the same total exposure given at one time, and that when the illumination was very weak it did not yield the calculated amount of effect compared with a more intense illumination. In the same year (Abney, Chemical Action and Exposure, Photo. Journal, 1893, xviii. 56) the proposition was discussed in greater detail. It had been stated by Bunsen and Roscoe (Pogg. Ann. xc. 96, 373; c. 43, 481; 1855–1859, ci. 255; cviii. 193) that what was termed the *Reciprocity Law* (It=E, where I is the intensity, t the time, and E the exposure) holds good for photo-chemical reactions independently of the values assigned to I and t. This was proved by Abney not to be true, that in fact, the law was not valid for photographic emulsion surfaces.

The effect produced by exposure might depend upon the value of the components, time and intensity, or might be dependent upon the absolute value of the product It. Abney found that with the slower sensitive surfaces then available (1893) that the actual intensity of the light produced marked differences of effect, but that these differences became less marked as the more sensitive surfaces were employed. With respect to intermittent exposures, Abney's experiments showed that the sum of a series of short intermittent exposures was not equal to a single exposure of the same total duration, the intensity of the light falling on the surface remaining constant, and that the apparent loss in the exposure increased by diminution of the intensity of the light. With respect to the total effect, the effect of duration of the separate exposure in relation to the duration of the period of rest between successive exposures, was considered, and it was found that when the exposure period decreased in respect to the period of rest the effect diminished, although the total exposure was constant. When the length of each exposure was varied, when the ratio of the interval of exposure to the rest period did not alter, it was found that the absolute duration produces a difference in result, the effect increasing with the absolute duration. If the exposure periods were equal in amount, but the intervals of rest differed, on the latter being diminished, the effect of the former is increased, viz. as the exposure suffers less break in continuity, the effect approaches that of a continuous exposure of the same duration.

The experiments yielding the foregoing results were made with light of moderate initial intensity, but the author found that the effects, when a very intense light was employed, approximated, that there was, in fact, in both cases a failure of the Bunsen-Roscoe law. Abney considered as a consequence that there would be one intensity which would yield an optimum effect. He found that the more intense the light the flatter became the curve of gradation, viz. less contrast. Further, that 'if the intensity of the light is increased beyond a certain limit, the product of intensity and time being kept constant, the energy used up in the work of chemical decomposition diminishes'; and from his experiments came to the final conclusion that for each individual plate there is a light intensity which yields a maximum effect with a particular exposure, and that on either side of this value the useful energy decreases (*see* Abney, J. Camera Club, March-April, 1894; Treatise on Photography, 10th ed. London, 1901, 399–405).

Eder (Jahrbuch, 1899, 457, and Schwartzschild, Photo. Correspondenz, 1899, xxxvi. 190, 171) confirmed the observations of Abney, and the latter proposed a modification of the Bunsen-Roscoe Law, putting It^p=E, p having a value slightly less than unity. Abney had, however, shown that p was not constant, and with this Englisch (Über die Workung intermittender Belichtungen auf Bromsilber Gelatine, Archiv. wiss. Photo. i. 117; Das Schwarzungs-gesetz, Knapp, Halle) was in agreement. The subject has been since that time examined by Sheppard and Mees (Investigations on the Theory of the Photographic Process, London, 1907, 214), by Wallace and Lemen (Astrophy, J. 1909, xxix. No. 2), by A. Werner (Zeits. f. wiss. Photo. 1908), by Renwick (Photo. Journal, 1912, lii. 260), by Channon (*ibid.* 1920, lx. 164), and by Slade and Higson (Proc. Roy. Soc. 1920, A98, 154).

Sheppard and Mees considered the problem as to whether the effect was proportional to t, and found that it was not a simple function of that quantity, agreeing with Englisch, and that the total value of It does not influence the failure, but were not able to agree with Abney from their own experiments as to the difference with sensitive materials of different speeds, but admit that their results required confirmation. These investigators found also the intermittency error.

According to Kron (E. Kron, Über das Schwartzungsgesetz photographischen Platten, Eder's Jahrbuch, 1914, 6) the reciprocity law holds good for a time scale, but not for an intensity scale.

Renwick (Photo. Journal, 1916, lvi. 11),

in a brief but clear and helpful note on Schwartzschild's Rule following considerable experience, draws attention to the fact that the components I and t, and not alone their product, affect the magnitude of the result and speaks of the neglect of the rule in practical photography. This is quite true, but many serious practical negative makers, nevertheless, have long been aware of the fact, and in past years, when surfaces were much less sensitive than are those in general use to-day, it was always recognised that camera exposures with reduced apertures could not be gauged by considering lens aperture area alone, for with diminution of illumination resulting from reduced lens aperture, exposure must always be increased apparently disproportionately to the reduced brightness of image, which is Schwartzschild's Rule in application.

Instead of p Renwick takes its reciprocal, which he designates q, the value of which factor varies between 1·1 and 1·2 with 1·16 as a fair average value for the rapid dry plates of to-day, and proceeds to show the application of the rule in an instance pertinent to photographic practice.

Considering an exposure of n seconds to light of intensity I, what is the corresponding exposure period if the intensity be changed to i? The first exposure $=n$I, but by the rule for equal effect, $n\mathrm{I}^q$ must be equal to xi^q, hence x, the required time of exposure, $= n\left(\frac{\mathrm{I}}{i}\right)^q$. Taking $q=1{\cdot}16$ the author gives the following instructive table:—

$\frac{i}{\mathrm{I}}$	Approximate exposure times for intensity i
1	n
1/5	$6{\cdot}5n$
1/10	$14{\cdot}5n$
1/20	$32{\cdot}3n$
1/30	$51{\cdot}7n$
1/60	$115n$
1/300	$747n$

In the same communication is discussed the rule in relation to the determination of the value of gamma (development factor) and the inertia of a plate according to the system of Hurter and Driffield (*q.v.*).

Upon the most recent consideration of the failure of the Bunsen-Roscoe Law, Slade and Higson found that for high light intensities the effect is proportional to the intensity with constant time, whereas, for low intensities the effect is proportional to the intensity squared, and they find differences in this respect between homogeneous and heterogeneous light. With reference to the latter it is observed that Wallace (*l.c.*) made a similar suggestion in 1908.

For a fairly full discussion of this subject, especially with respect to fundamentals, *see* F. E. Ross, Relation between Photographic Density, Light Intensity and Exposure Time, J. Opt. Soc. America, 1920, iv. 255.

Effect of temperature on the sensitiveness of the dry plate.—With reference to the formation of a *visible* image, Bunsen and Roscoe found that variations in temperature did not influence the rapidity of darkening of silver chloride paper (containing free silver nitrate) in light. Eder (Modern Dry Plates, 1881) observed that temperature variations between 5°–25°C. had no effect on the formation of the latent image on silver bromide plates 'so long as one and the same temperature prevails after exposure and during development.'

The question of the influence of temperature on photographic action appears to have remained in this condition until 1884, when greater consideration began to be paid to the matter, in so far as developable as against 'print out' surfaces were concerned, the latter not having received attention. In 1884, Abney (Photo. Journal, viii. 128) showed that so far as silver bromide (collodion emulsion and gelatine dry plates) were concerned, temperature had a marked influence on sensitiveness, and that by heating a plate and exposing in that condition greater photographic action resulted as against a similar surface cold, and, that this result was not due to the elimination of water from the film. Dewer (Royal Institution) showed that the photographic image is formed at temperatures near to zero absolute, for at −180°C. 20 p.c., and at −252°C. 10 p.c. of the normal photographic effect took place. In 1895, Abney again dealt with the problem and, more precisely (J. Chem. Soc. ix. 103; Photo. Journal, 1895, xix. 378), finding that heat increased the apparent rapidity of a plate with time exposures and the steepness of gradation with intensity exposures, the temperatures of observation varying between −18·5°C. and 33°C. The subject received attention later from Wallace (On the sensitiveness of Photographic Plates at different temperatures, Astrophy. J. 1908, xxvii.; Brit. J. Photo. 1909, lv. 661) particularly with regard to stellar photography, and the paper, with its considerable detail and its conclusions, will well repay study.

The photometric constant.—It has been stated by Hurter and Driffield (*q.v.*, p. 234), that the quantity of silver in a negative per unit area is strictly proportional to the density D. The authors found that the actual mass in grammes on 100 sq. cm. was equal to PD, where P is a constant, being the mass in grammes required to produce unit density per 100 sq. cm. They gave as the value for P, 0·0121 for a range of density values from 0·5 to 2, for ferrous oxalate development (*see* Sector and Grease Spot Photometers, J. Soc. Chem. Ind. 1891, x. No. 1), and later (The Latent Image and its Development, Photo. Journal, 1898, xxii. 190) a new figure, 0·0131, the value varying slightly with different developers, especially if there be any stain. Eder found for ferrous oxalate P=0·0103. Sheppard and Mees (Theory of the Photographic Process, London, 1907, 39–43) redetermined the constant and obtained a mean value for densities varying between 2·4 and 3·25 of 0·01031 for ferrous oxalate, and considering the differences between their values and those of Hurter and Driffield, observed that there is a probability that the state of emulsification has influence upon the silver deposited on development. Nutting (Washington, Acad. Sci. J. 1913, iii. 322) considered the subject mathematically, and came to the conclusion that grain size would affect the constant. Slade (Faraday Soc. Trans. 1920, xv.) in a theoretical discussion confirmed the constancy of P, but did not make any allowance for grain size. Higson has developed the method of Slade (Photo. Journal,

1920, lx. 161), concluding 'that P depends on both the diameter of the grains and their effective specific gravity, and can only be accidentally constant for various silver deposits.' This investigator gives the following values of P for certain assumed size of grain in microns: 1μ, P=0·0061, 2μ, P=0·0122, 3μ, P=0·0183.

Later, Mees (J. Frankl. Inst. 1921, cxci. 631), discussing the structure of the photographic image, considers how far P is dependent upon grain size, and further as to whether it is altogether independent of their distribution in the film, which problems, he considers, have yet to be settled by experiment, making the preliminary assumption that where the same mass of silver is distributed differently through the same film, that P may also be different, and gives as a case deposits of the same optical density which have been produced by ultra-violet light in one instance and by X-rays in another. In an abstract of his paper the author, taking these instances, states that—

'In the first case, the grains of silver forming the image would be entirely upon the surface of the emulsion, while in the second they would be distributed uniformly throughout the depth of the emulsion. It would seem probable that in the second case, where the packing was not nearly so close, a greater mass of silver would be required for the same density than in the first case, where the grains are packed in the surface layer. If this is true for such an extreme case, it will also be true, though to a less degree, for images produced by light of different colours, since the penetration depends upon the wave-length of the light, and an image produced by red light, for instance, will be distributed to a greater depth in the emulsion than one produced by violet light' (Abridged Scientific Publications, Research Laboratory of the Eastman Kodak Co., iv., No. 109).

The Hurter and Driffield system.—Although scattered throughout the early literature of photography may be found references to the fundamental problem of the relation which the silver deposits in the finished negative bore to the light intensities of the corresponding parts of the optical image to which the sensitive photographic surface had been submitted in the camera, it was not until 1890, when Hurter and Driffield (Hurter, Ferdinand, and V. C. Driffield, Photo. Chemical Investigations and a new method of determination of the sensitiveness of Photographic Plates, J. Soc. Chem. Ind. 1890, ix. 455–469) published their important paper, that the matter received serious attention. The investigations in this communication and later papers laid the foundation of the modern quantitative study of photographic problems (*see* the Memorial Volume, The Photographic Researches of Ferdinand Hurter and Vero C. Driffield, London, 1920, xii. 374, Royal Photographic Society).

The authors asked themselves at the outset, 'What is a perfect negative?' and stated that—

'A negative is theoretically perfect when the amount of light transmitted through its various gradations is in inverse ratio to that which the corresponding parts of the original subject sent out.

'The negative is mathematically the true inverse of the original when the opacities of its gradations are proportional to the light reflected by those parts of the original which they represent.'

Considering the absorption of light by opaque black substances, they defined the terms *opacity*, *transparency*, and *density* of a negative, which they denoted respectively by the letters O. T. and D., and stated that, for substances which do not reflect much white light, the relations between the light that is absorbed from an incident pencil and the quantity of the substance present, which exercises that influence, is simple. Considering a uniform layer of such a body—Indian ink—they imagined this layer to absorb one-half of the incident light, then the light transmitted is one-half of the intensity of the original pencil. Two such layers reduce the intensity to one-quarter, and so on, and that—

'In general any number of layers would reduce the intensity of the light to a fraction, which is equal to the fraction the first layer allows to pass, but raised to a power, the index of which is the number of layers employed. If n equal layers were employed, and the first one reduced the intensity of the light to a fraction $\frac{I}{m}$, the n layers would reduce it to $\left(\frac{I}{m}\right)^n$.

'If instead of using so many successive layers, the first layer was made to contain as much Indian ink as the n successive layers contain altogether, we should find that the one layer now reduces the intensity of light by exactly the same amount as the n layers did. The reduction of the intensity is, of course, due to the black particles, and depends simply upon the number of them which are interposed per unit of area. We can thus replace the number of layers by the number of particles.'

The investigators employed as their source of radiant energy the 'British Standard' candle, and regulated the intensities of light falling upon the sensitive surface by means of a rotating disc with angular openings in geometrical progression, so that the intensities were as 1 : 2 : 4 : 8, &c. Upon development—and any other subsequent procedure upon the developed image by which the deposit was affected—the opacity of the deposits were measured in what was essentially a Bunsen photometer.[1]

The principles enunciated, the methods employed for their verification, and the application of these principles, in so far as they related to photographic problems, came to be known briefly as the 'Hurter and Driffield System.'

When a sensitive surface, such as that constituting the photographic plate, is exposed to a geometrically progressing series of light intensities: 1 : 2 : 4 : 8 : 16, &c., and the deposits in the resulting negative formed by development be measured (optically) in a suitable photometer, on plotting the densities so obtained against the exposure logs there is produced an $\int$ shape curve, which Hurter and Driffield called the 'characteristic curve of the photographic plate.'

From the curve so produced is found the capacity of a plate to record correctly the different light intensities to which it was

[1] The first recorded work upon the measurement of the opacity of the developed photographic image is that of Abney, who described his method in 1874 (*see* Phil. Mag. Sep. 1874, xlviii. S4, 317).

originally exposed. If the plate is capable of recording correctly these different intensities, it follows that there must be a simple relationship existing between the light intensity acting (exposure) and the opacities of the resulting negative.

This leads to the following definition: When a negative is theoretically perfect the amount of light transmitted by its various gradations will be in inverse ratio to that which the corresponding parts emitted. Further, the negative is mathematically the true inverse of the original when the opacities of its gradations are proportional to the light reflected by those parts of the original which they represent.

The 'exposure' is defined as the product It, I being the light intensity and t the time of exposure thereto.

The source of light the investigators used, the 'British Standard' candle, as stated, was placed at a distance of one metre from the sensitive surface, the unit period of exposure being one second. The results of such exposures were given in candle metre seconds (C.M.S.).

The density D, or the silver reduced on development, is dependent on the time of exposure and the degree of development it receives.

The authors stated that the density D is the log of the opacity O, or the anti-log of the transparency T.

The relationship may be summarised as follows:—

$$\text{Transparency } T = \frac{\text{intensity of light transmitted}}{\text{intensity of light incident}} = \frac{I}{I_0}$$

$$\text{Opacity } O = \frac{\text{intensity of incident light}}{\text{intensity of transmitted light}} = \frac{I_0}{I}$$

$$\text{Density } D = -\log_{10} T = \log_{10} O$$

The opacity of a substance is its optical property impeding the passage of light through it, the case in consideration being silver, thus the opacity of a deposit of silver transmitting $\frac{1}{10}$th of the original light would be 10.

The transparency of a substance is its optical property representing the amount of light not impeded in its passage through a substance.

The density is the relative quantity of silver per unit area, and forms the connection between exposure and opacity. The following scheme represents this relation:—

Intensity incident light.	Absorbing layers.	$\frac{i}{T}$	Opacity O	Density D
100	I	10	10	1
100	II	1	100	2
100	III	0·1	1000	3

It will be seen from the relationship expressed that the density is the logarithm of the opacity, and in a theoretically perfect negative the opacities are proportional to the light intensities producing them, and therefore each density must be proportional to the logarithm of the light intensity producing it, or in other words, the density is a linear function of the logarithm of the intensity of the light and the time of exposure.

From this it follows that while the light intensities progress geometrically the densities, or silver deposited, will progress arithmetically,

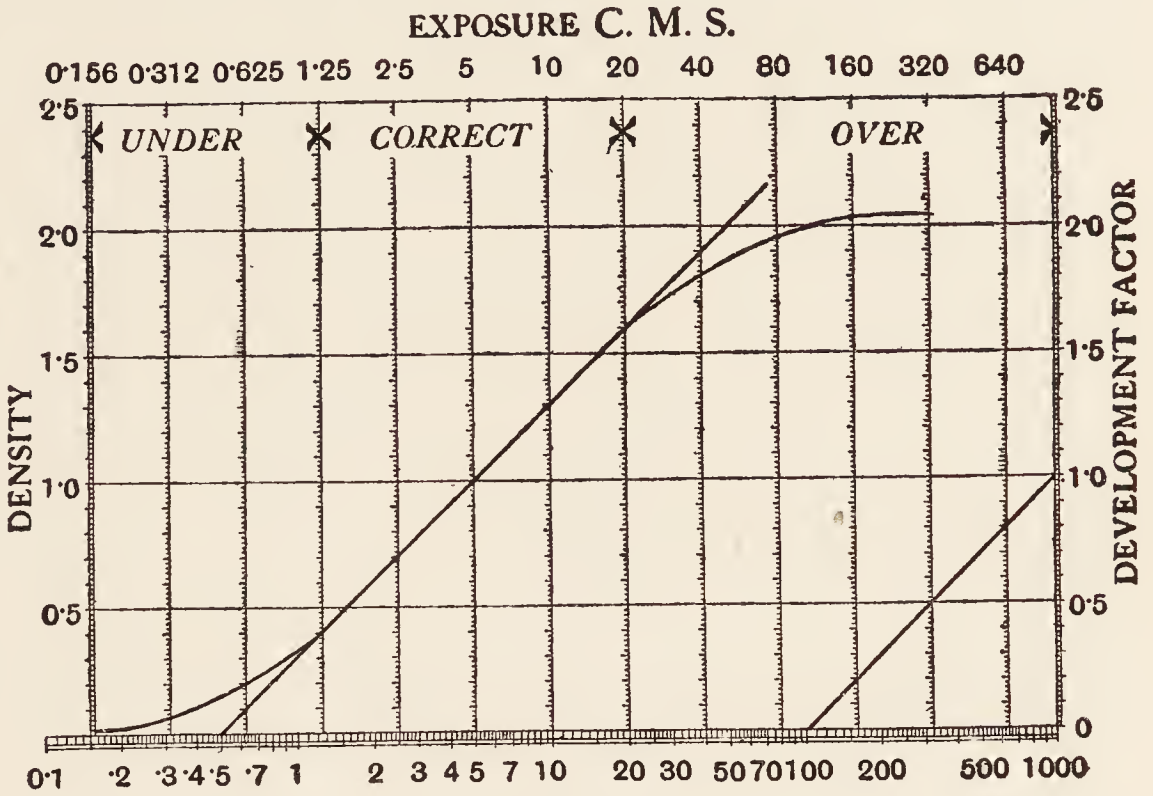


FIG. 1.

and the opacities of the deposits geometrically.

In Fig. 1, representing the characteristic curve, it is observed that the foot and the top are inflected, the centre being a straight line. These periods respectively represent, the under, the over, and the correct periods of exposure.

If on producing the straight line period so as to cut the exposure scale, or log E axis, the point of intersection is called the 'inertia' of the plate, or a measure of its slowness, and this is constant with a given plate.

As a numerical value of the speed [1] of the plate, Hurter and Driffield divided a constant 34 by the inertia $=\frac{34}{i}$, and therefore the greater the value of i the lower the speed, and conversely the lower the value of i the greater the speed, the inertia being expressed in candle metre seconds.

Thus, if we assume the intersection on the log E axis to be $\bar{1}\cdot397=0\cdot25$ cms., the speed of the plate would be $\frac{34}{0\cdot25}=136$ (H. and D.).

Further, the straight line portion (showing equal rise) of the curve—the correct period of exposure—in practice, represents the range of exposure through which a given plate is capable of faithfully recording, thereby determining the

[1] This was the *actinograph* speed, but eventually the word actinograph ceased to be used (*see* The Actinograph, Photo. Soc. Reporter, April, 1889; Memorial Volume (*see ante*), 57).

latitude, or variation, in exposure which may be allowed without disturbing the 'constant density ratio.'

By 'constant density ratio' is meant that, no matter what the exposure may be, so long as the range of intensities fall within the correct period of representation, the densities so produced for equal development will bear the same ratio though the deposits vary considerably.

The density of the deposit D is, in practice, the variable quantity, and is dependent on many factors.

Higson (Photo. Journal, 1921, lxi. 35) has stated that the factors which determine the 'blackening' of the plate are as follows:—

(1) The photo-chemical law of the AgBr grain.

(2) The size or sizes of the grain.

(3) The diminution of light intensity through the film.

(4) Development.

Of these, the one necessary for the present purpose is (4), and this in the final stage of practical operations is the factor determining the 'quality' of the photographic negative.

Hurter and Driffield observed that in a theoretically perfect negative the opacities of the different gradations were strictly proportional to the light reflected by the object they represented when the plate had received 'correct' exposure, and that a true representation of the tones of the original is only possible when the density or quantity of silver is proportional to the logarithm of the light intensity producing this density.

This being the case, it follows that in a correctly exposed and correctly developed negative the densities will be equal to the logarithms of the exposure, and when such is the case the tangent of angle (formed by a continuation of the straight line portion of the plotted curve with the abscissæ) will be 1, the angle being 45°.

This figure of value is known as the *development factor* of the plate, generally called the gamma, γ, and is variable according to the grains constituting the sensitive material, the number present, their reducibility, the potential of the reducing ion, the concentration, the diffusibility, and the time and temperature of the developer.

If, then, D represents the amount of silver that can be reduced of a given series of grains, the maximum contrast will be attained at maximum development, or γ_∞ (*gamma* infinity), and this factor varies considerably in different emulsions. *Gamma* is frequently termed the contrast factor.

In actual practice in sensitometric work it is usual to calculate this limiting factor, and Sheppard and Mees showed that if two sensitometric strips be developed for such times that one is double the other, and that $\frac{\gamma_2}{\gamma_1}$ does not exceed 1·8, the following formula will give reliable figures:—

$$\frac{{\gamma_1}^2}{2\gamma_1-\gamma_2}=\gamma\infty$$

The rate at which the plate develops, or its velocity constant, K of development, as has been noted, varies according to several factors; for a given reducing agent, however, over a large range of development, though t (time) and D (density) vary, it remains unchanged, and represents the fraction of the original density $(D_\infty - D)$ that will be developed in the unit of time, providing always the conditions be kept constant. As in the case of the development factor, the velocity constant K will vary considerably in different emulsions, usually being greater with slow plates than with rapid ones.

In making sensitometric observations it is usual to adopt a standard light, and as already noted, the Standard Candle was adopted originally. Hurter and Driffield, however, recognised that it was not ideal, but sufficient for their purpose in establishing the laws which govern the production of a photographic negative.

The question of light standards has been fully investigated by Sheppard and Mees (*see* Investigations on the Theory of Photographic Process, London, 1907, Photo. Journal, 1910, l. 287; Renwick, *ibid.* 1910, l. 157).

Sheppard and Mees adopted the Fèrey (J. de Phys. 1908, iv. 632) standard acetylene flame, which is a cylindrical column of flame, burned in a specially designed lamp, a section of the flame being employed which showed little variation in use. The light was carefully screened so as to approximate to daylight, so that, in comparing the relative speed between non-colour sensitive (ordinary) and colour sensitive (orthochromatic and panchromatic) plates the results were not vitiated by differences in spectral distribution.

It is, however, essential that the actinic value be determined photographically in terms of the standard candle.

The apparatus for the exposing of the plate to a graduated series of light intensities consisted originally in a series of angular apertures cut in a disc of suitable material, and when rotated at a high speed gave the required gradations. Such discs, or sector wheels, were cut with angular segments, generally eight or nine in number, each angle being twice the value of the preceding one.

Much research and discussion has been raised on the relative value and merits of exposure machines, especially those of the sector-wheel type, it being found that the photographic surface does not in general integrate the intermittent exposure.[1] It is now recognised that it is preferable to use scales of intensity (light transmitted through a neutral tinted wedge, for example, *see* E. Goldberg, 11th Int. Congress Photography, 1910, Report, 152; Brit. J. Photo. 1910, lxvii. 648), and by means of moving slotted plates (*see* L. A. Jones, A New non-intermittent sensitometer, J. Frank. Inst. 1920, clxxxix. 303, also Photo. Journal), keeping the time constant instead of varying the time factor and not the intensity.

Having exposed the plate under suitable conditions, it is usual to carry out development with a developer which does not stain, omitting soluble bromide, and maintaining the solution

[1] The researches on this problem are considerable; for details the reader should consult the Bibliography in the Photographic Researches of Hurter and Driffield (Memorial volume, *see ante*); Odencrants (Zeit. wiss. Photo. 1919, xviii. 210); Higson (Photo. Journal, 1920, lx.), as well as the other authorities cited from time to time in this section.

at a constant temperature. After development the plate is fixed, washed, dried, and is then ready for measurement.

Instruments for measurement of densities (photometers) are numerous, but it is of importance to observe that considerable difference will arise in these determinations, according to whether the densities are determined in diffused light, $d\,\#$, or parallel light, $d\,\|$, since it must be noted that not only do photographic negatives absorb, but also scatter, light, this apparently first having been observed by Abney.

In making determinations of speed it is necessary that the density plotted should be minus fog; this may be done by placing a fog strip from the developed plate in the path of the light against which the densities are determined, or it may be separately determined, and deducted from the final result (J. Soc. Chem. Ind. 1890, ix. 722); Callier (Photo. Journal, 1909, xlix. 198); Ferguson (*ibid.* 1912, lii. 183); Ferguson, Renwick and Benson (*ibid.* 1918, lviii. 155); Sheppard and Mees (Investigation on the Theory of Photographic Process (Longmans)).

In discussing the exposure problem Hurter and Driffield observed that correct exposure was imperative, and that the periods of under and over exposure were of little or no value. Of under exposure they said—

'The characteristic of this period is a negative in which the shadows, and nearly all the half tones, are almost bare glass; the high lights being marked by relatively extreme density.'

This may or may not have been correct, but the fact must not be overlooked that at the period at which their communications were made, the chief printing processes consisted of salted paper (albumen), gelatino-chloride (P.O.P.), carbon (bichromated gelatine), iron such as platinotype papers which were of different scales of gradation than those now in vogue.

They gave also in their original paper (*see ante*) formulæ, showing that in this period the density is almost proportional to exposure, *i.e.* $D=\mu It$,

where D= density, or opacity logarithm of the silver deposit.
μ=a constant.
I=light intensity acting.
t=time of exposure thereto.

Modern bromide papers (silver bromide) in their multitudinous conditions, and later the perfection of gaslight papers (silver chloride), have led to a reconsideration of the under-exposure period.

Renwick (Brit. Journ. Photo. 1912, lxix. 289, 312) advanced the opinion that the under-exposure period of the characteristic curve of an emulsion was of greatest importance, since in practical photography we are compelled to use it in making the final positive, and later to confirm the accuracy of the statement (Photo. Journal, 1913, liii. 127), developed the mathematical treatment of the subject, giving conclusive reasons as to its value, which are undoubtedly valid in practice.

Later, Higson (Photo. Journal, 1921, lxi. 144, 'The Action of Light on the Photographic Plate, Under-exposure Period, Part II.') has observed that the under-exposure period should be as much a characteristic of any plate as the inertia, and therefore a measure of its speed, and obtained data from unpublished extensive experimental work of Grundy in support of his theoretical conclusions.

Of the over-exposure period Hurter and Driffield said: 'the tendency of the gradations in the case of over-exposure is to approach one uniform density,' and hence what would be called a flat negative.

This period is of relatively little importance, since the bane of all modern photography is the unreasoning desire for speed, and, in consequence, the great tendency is to under-exposure. Usually a good photographic emulsion is so constituted so as to ensure a longer scale of gradation than will be required in practical use.

Apart from its use in the determination of plate speeds and other constants, and now largely used in plate manufacture, the Hurter and Driffield system is of great value in the determination of the problems in development, intensification, and reduction, and numerous questions affecting the silver halide grain of the photographic emulsion.

The work carried out by numerous investigators on the action of light on the sensitive surface is very extensive, for which the Bibliography in the Hurter and Driffield Memorial Volume (*see ante*) should be consulted. Since the publication of this volume, Ross (Journ. Opt. Soc. Amer. 1920, iv. 255) and Higson (Photo. Journ. 1921, lxi. 35, 144) have added valuable contributions, the latter following an investigation on the Photo-chemical Laws of the Silver Halide Grain (Slade and Higson), which is largely mathematical. More recently Higson and Toy (Photo. Journal, 1923, lxiii.) have considered the different factors which affect the constant, *gamma infinity*, and give certain conclusions as to the influence of grain size and the developer.

For a recent contribution to the sensitometry of photographic sensitive surfaces, *see* Paper No. 439, 1922, issued by the United States Bureau of Standards, Washington, which records a series of investigations on the constants of a large number of plates and films made in the United States, by Davis and Walters of the Bureau staff.

For the section of this article dealing with the 'Hurter and Driffield' system the author is indebted to the courtesy of Mr. J. Willis Grundy, himself a worker of considerable experience in the subject.

Development of the Exposed Sensitive Surface.

To render visible the action of light the exposed surface is 'developed,' the process consisting essentially in reducing to silver those portions of the silver halide which have been affected by light, whilst leaving those not so affected unchanged.

Development is effected by the application of a reducer which generally consists of an aqueous alkaline solution of certain phenolic derivatives, of which the most important are *pyrogallol*, *quinol*, *metol* (monomethyl *p*-aminophenol sulphate), and *p*-aminophenol. *Amidol*

(diaminophenol hydrochloride) is used in aqueous solution of sodium sulphite alone. The alkali used is generally sodium or potassium carbonate or the corresponding hydroxides.

The degree of alkalinity necessary in the solution differs with the reducer. It is at least necessary to have the solution alkaline to litmus, and certain of the reducers employed will develop when the solution is in this condition. Thus, pyrogallol will develop in a solution containing sodium sulphite free from carbonate, which shows the minimum alkalinity, but the action is extremely slow, but becomes more rapid if an alkali bicarbonate be used. Amidol will develop energetically, however, in a solution of sodium sulphite—free from carbonate—alone. It is a practice with most agents other than amidol to have a solution alkaline to phenolthalein, and for this purpose the alkali hydroxides and the normal alkali carbonates are employed.

The sodium sulphite is used as a preservative of the phenol derivative when a 'stock' solution of the developer is kept. Further, it acts as a preventitive of the discoloration of the solution during development. Under this condition the stain image (*see ante*, p. 227) is less than in its absence, indeed, the concentration of the alkali sulphite is the controlling factor in this respect. The difference in colour of the solution, due to the presence of sulphite, is probably because the oxidation products are not the same. Excess of sodium sulphite leads to the production of 'fog' (Mees and Piper, Photo. Journal, 1911, li. 234; *ibid.* 1912, lii. 221).

In practically every developing solution there is present an alkali bromide, generally the potassium salt, the purpose of such agent being to restrain development and to act as a preventitive of 'fog.'

In a simple case of development of an exposed plate, for example, with a solution of quinol and alkali alone, the particle of the silver halide reduced yields metallic silver, an alkali bromide, and the oxidation product of the reducer, viz. quinone. The action is reversible, for if a silver image be treated with a solution of quinone and an alkali bromide, an image in silver bromide with quinol in solution results.

It is a common observation that the rate at which images appear varies with different reducers. Eder has made a simple classification according to these differences:

(*a*) those reducers where the tones develop gradually step by step according to their brightness; and

(*b*) those reducers where the tones appear practically at once and afterwards gain density to represent the brightness.

In group (*a*) pyrogallol and quinol may be placed, whilst into group (*b*) amidol, metol, and *p*-aminophenol fall.

The rate of development declines as development progresses until a limit of density is reached. According to Hurter and Driffield this rate is proportional to the quantity of the developable halide remaining before the limit is reached. When the reducer diffuses into the emulsion film and reaches the halide grain the silver salt passes into solution and is ionised, reaction then occurs between the ion of the reducer aud the silver ion, the latter loses its charge, producing silver in solution, which solution soon becomes saturated and equilibrium is attained. In the presence of a nucleus on which the silver can be precipitated this equilibrium is not maintained, and the action proceeds until the grain is wholly reduced. The difference between unexposed and exposed silver halide is shown by the fact that one will develop and the other will not, and the action of light, whatever it may be, is to produce that difference, the nucleus which will provide the deposition centre in the grain for precipitated silver. The most recent assumption as to the nature of the latent image in a modern high-speed dry plate is that in the ripened emulsion there exists a very unstable form of colloidal silver in solid solution in the grains, and this becomes precipitated by light action in the gel form, and that the coagulated particles act as nuclei during development (*see* Renwick, Photographic Images Visible and Invisible,[1] J. Soc. Chem. Ind. 1920, xxxix. T.); but this view has been contested by Luppo-Cramer (Photo. Correspondenz, 1920, lxvii. 259, 285); and by Sheppard (Brit. J. Photo. 1921, lxviii. 4); *see* Renwick's remarks (Brit. J. Photo. 1922, lxix. 370).

The rate, or velocity, with which development proceeds differs with different reducers. Analogy has been made to Ohms Law, writing $\text{velocity} = \frac{\text{potential}}{\text{resistance}}$, so that if the rate be measured and we could also measure the resistance we could obtain the potential, and this would be a measure of the developing power of the reducer. This would be the *reduction potential* (R.P.), or a measure of the energy of the developer (*see* A. H. Neitz, Recent Investigations on the Theory of Development, Photo. Journal, 1920, lx. 289).

Now, Hurter and Driffield pointed out that when a soluble alkali bromide is added to a developer there is an increase in the inertia of the surface under development. Neitz (*l.c.*) observes that this effect is conditioned by the R.P. of the developer, and that when the value of the R.P. is low, a given bromide concentration will lower density more than if the R.P. be high, exclusive of the effect of the bromide on 'fog.' Developers vary considerably in the value of their R.P.'s, and the author has measured these values for a large number of developers by 'the depression in density produced by a given bromide concentration, or by the concentration of developer against which a developer can just develop.'

It has been shown that maximum density attainable tends to increase with the R.P. value, but that maximum is not *correlated* with the R.P. A definite relation has not been established between R.P. and the time of appearance of the image, nor is the 'fogging' power of a developer a function of its R.P.

[1] This paper contains, in addition to its own valuable contribution to the study of the causes which lead to the formation of the latent photographic image, a most comprehensive bibliography of the serious literature on this subject. Since the date of its publication several additional communications have been made by different workers, amongst which are: M. Volmer, Zeit. wiss. Phot. 1921, xx. 189; J. Soc. Chem. Ind. 1921, 239*a*; Sheppard and Trivelli, Photo. Journal, 1921, lxi. 400; J. Brooksbank, *ibid.* 421; Svedberg, *ibid.* 1922, lxii. 183–192, 186–192.

The highest effective plate speed appears to be secured with a developer with a high R.P. if sufficient bromide be used to eliminate 'fog.' The effect of bromide on the rate of development occurs during the early stages of development, in the 'period of induction' (*see* Sheppard and Meyer, Chemical Induction in Photographic Development, Photo. Journal, 1920, lx. 12). When this period is passed the bromide does not affect the rate.

Nietz observes as the result of his research that 'the ordinary practical working properties of a developer are not satisfactory criteria of its relative energy.' As a guide to the elucidation of the 'practical working properties' of a developer, *see* the useful paper by J. P. Crabtree, (Photographic Methods of Testing Developers, Brit. J. Photo. 1922, lxix. 153, 170, 188).

The simple general results of the relation of development to light action have been discussed under the Hurter and Driffield system, p. 234.

With respect to the determination in practical photography of the correct time of development for the desired degree of contrast, three methods are employed: (*a*) judgment by visual examination, (*b*) factor, (*c*) by time.

The method (*a*) is adopted by a large number of photographers, but in view of its uncertainty from various causes it has given rise to considerable objection from time to time. The factorial method (*b*) was first introduced by Watkins, 1894 (Brit. J. Photo. 1894, xli. 697), when the author showed that the development period with a particular developer might be measured by the time of appearance of the image, *i.e.* the time which elapses between the application of the developer and the appearance of the image, and that, for a particular range of contrast the total time of development required was a multiple of the time of appearance. The method is a most helpful aid in practical photography (*see* Watkins, Photography: Principles and Applications).

In the method (*c*) development is based upon a predetermined time. With a particular kind of emulsion a developing solution of a particular composition and at a certain temperature will take a specified time in order that the developed image may present a particular degree of contrast. The rate of development at a particular temperature varies for different plates and for the various batches of the same kind of plate, and this introduces difficulties, and although by means of the temperature coefficient the times of development for different temperatures may be calculated, these only hold for small temperature variations. The method may be very usefully applied if the time required for a given degree of contrast be ascertained for any particular batch of plates. Tank development is an application of the time method, a relatively dilute solution being employed.

The following papers contain valuable information with respect to the technology of development: A. Watkins, Time Development, Photo. Journal, 1909, xlix, 367; Variation in Temperature Coefficient, *ibid.* 1910, l. 411; Mees, Time Development, Photo. Journal, 1910, l. 403; Mees and Piper, Fogging Power of Developers, Photo. Journal, 1911, li. 226; *ibid.* 1912, lii. 221; W. B. Ferguson and B. F. Howard, Control of Times of Development at various Temperatures, Photo. Journal, 1905, xlv. 118; W. B. Ferguson, *ibid.* 1906, xlvi. 182; Temperature coefficient for Pyro Soda Developer, *ibid.* 1910, l. 412; J. C. Kingdon, Causes in the Variation of the Watkin's Factor for different Developers, Photo. Journal, 1918, lviii. 270, and Sheppard, *ibid.* lix. 135; F. W. T. Krohn, Mechanism of Development, Photo. Journal, 1918, lviii. 179.

Desensitising the Exposed Photographic Surface Prior to Development.

The high degree of sensitiveness of many modern dry plates entails very reduced illumination in the dark room, and any procedure which would avoid the necessity for this is a gain in practice. In 1898, Mercier (Compt. rend. cxxvi. (21), 1500; J. Soc. Chem. Ind. 692*a*) proposed treating an exposed plate with solutions of certain developing substances, which when followed by drying rendered it possible to correct for over exposure. The principle of this suggestion occupied later the attention of Luppo-Cramer, who showed (Photographische Correspondenz, July, 1901) that the effect was due to a desensitising of the emulsion film, and that this was a property of a certain class of developing agent, notably *p*-aminophenols, and that the depression was sufficient to enable a plate to be developed in a light of such intensity that were the plate not so treated it would 'fog.' In 1907, Lumière and Seyewetz examined Luppo-Cramer's work, and they stated (Brit. J. Photo. 1907, liv. 633) that wetting the exposed plate was sufficient to produce reduced sensitiveness, and that this effect is due to the absorption of light by the layer of liquid covering the plate. Subsequently Luppo-Cramer disputed this view, stating that the fall in sensitiveness was only slight, but that, on the other hand, certain developers produced a marked depression, and that the effect was largely inhibited by the presence of sodium sulphite. As depressents, Luppo-Cramer gave plain aqueous 0·05 p.c. solutions of the hydrochlorides of diaminophenol ('amidol'), triaminophenol and triaminobenzol and triaminotoluol. With the salts of diaminophenol and triaminotoluol there ensued a fall in sensitiveness to 1/200 and 1/600 of the original value, respectively. By a preliminary treatment with a 1 : 2000 solution of triaminotoluol hydrochloride for a minute, a rapid dry plate may afterwards be developed in a bright yellow light. Eventually, Luppo-Cramer adopted an aqueous solution of Phenosafranine (1 : 2000). The plate after immersion in this solution for one minute in the dark may be developed subsequently in a fairly bright yellow light. The phenosafranine is effective, but the dyeing of the gelatine renders the removal of the colour tedious. The colour compound may also be added to the developer, in which case development may take place in yellow light, provided the plate be introduced to the solution in a 'safe' light. Luppo-Cramer observes that desensitisers act as mild oxidisers, preventing the formation of the 'latent' photographic image (Photo. Ind. 1921, 259, 312, 669, and J. Soc. Chem. Ind. 1921, xl. 325*a*; Die Phot. 1921, No. 3, I, No. 4, 18; Photo. Rundschau, 1921, 29, 37; J. Soc. Chem. Ind. 1921, xl.

324*a*). The phenosafranine does not destroy the existing image, but is effective in preventing the production of further nuclei by light action in the dark room when the agent is used as a desensitiser. An endeavour to meet the difficulty in accepting that an oxidation process takes place in the presence of a reducing solution of high potential (the developer) is made by Steigmann (Photo. Ind. 1921, 71–72), who suggests that in all similar cases the colour compound has been adsorbed by the silver salt, and by this process is withdrawn from the reducing environment. Many colour compounds in related and unrelated classes have been tried by Luppo-Cramer with varying results. In several instances 'fogging' takes place, and this appears to follow the use of basic compounds, but this feature may be overcome by the presence of acid colour compounds without nullifying the effect. Many colour compounds and other bodies have been examined by Lumière and Seyewetz (Brit. J. Photo. 1921, lxviii. 351, 370; J. Soc. Chem. Ind. 1921, xl. 529*a*; Bull. Soc. Fr. Photo. 1921, viii.; and J. Soc. Chem. Ind. 1921, xl. 718*a*) with respect to desensitising, and these workers have concluded that there does not appear to be any well-defined relation between their constitution and their ability to act as desensitisers. They considered that the best agent—barring the staining property—for very sensitive ordinary and panchromatic plates to be phenosafranine. When, however, complete desensitising of a red-sensitive film is not required Aurantia (ammonium salt of hexanitrodiphenylamine) is quite satisfactory. Similarly, a 1 p.c. solution of picric acid, a 2 p.c. solution of neutral potassium chromate, and 0·05 p.c. solution of chrysoidine may be used, the plate being treated for 30 seconds in either of these solutions before applying the developer, after which development may be in unscreened candle light. The advantage of the use of the latter agents is that they can be employed for paper where phenosafranine produces stain in the fibre. The effect of a number of inorganic bodies was tried, but in all cases, with the exception of neutral chromates, whilst acting as desensitisers, they destroyed the latent image. Luppo-Cramer has advocated the addition of phenosafranine to developing solutions in which the active agents are *glycin* (γ-oxyphenyl glycin) or *p-aminophenol* for development in bright yellow light (*see* Photo. Ind. 1921; Brit. J. Photo. 1921, lxviii. 321). The same investigator showed (Der. Phot. 1921, 65, 66; Brit. J. Photo. 1921, lxviii. 262) that by the addition of phenosafranine to a caustic quinol solution a developer of quick-acting character could be produced similar to *metol-quinol*, and at the same time development could proceed in a bright yellow light. This accelerating effect is contrary to that which occurs with some developers (pyrogallol and amidol, Crowther) when a retarding effect is produced. An advance was made in 1922 by König (Meister Lucius and Brüning) by the introduction of two new bodies for desensitising, *Pinakryptol* (a mixture of two colour compounds), *Pinakryptol green*, which do not permanently stain gelatine (*see* R. E. Crowther, Brit. J. Photo. 1922, lxix. 351).

The principal technical advantage of the use of a desensitiser will be found in the development of panchromatic plates. Without this aid very low non-actinic illumination of the dark room is necessary, which is to many workers a considerable source of inconvenience. Further, for the development of large numbers of ordinary plates, the system is a considerable aid, owing to ease in working in a bright light.

Intensification and Reduction of Developed Images.

The process of 'reduction' or of intensification is applied to negatives where there is either an excess or a deficiency in the general contrast of the picture, due either to defective manipulation or to the subject. There may in addition be a desire to alter the contrast to serve some particular purpose. A negative may sometimes suffer from an excess of density which unduly prolongs the time of printing, and reduction without alteration of contrast may be desired to avoid this inconvenience. A process of reduction (which is really one of oxidation) is one for the removal of some of the material of the image, either silver or stain body, by means of which the effective opacity (*see ante*, p. 227) is reduced, and of intensification, one by which the effective opacity is increased either by the addition of metal or other material, or by a change in the hue of the image substance. Experimental observation has shown that marked differences are obtainable by the employment of the various methods. The simplest case of intensification occurs in wet collodion (*q.v.*) where, by the application of a soluble salt of silver in the presence of a reducing agent, the image is built up by the same process that obtains in the original development. Again, the conversion of the dry plate image to a silver-mercurous chloride by the action of a solution of mercuric chloride followed by a developer as, for example, ferrous oxalate, will yield the original silver image, and an equivalent of mercury, and the opacity is increased. For reduction a simple process is to partially rehalogenise the image, afterwards converting the halide formed to a soluble salt (as by the action of sodium thiosulphate), which is removable by washing. Many methods are available for both processes, and it may be said that, *generally speaking*, they are suitable for both gelatine and collodion plates, with the proviso that the former is a medium that tends readily to stain. If a negative be *reduced*, presuming the final washing has been properly effected, the image may be regarded as at least as permanent as the original, but many processes of intensification are suspect in this respect and with good reason.

Probably the most satisfactory process for the intensification of dry plate images is the chromium method, where the silver is converted to a chloride in the presence of an alkali bichromate by means of a solution of potassium bichromate and hydrochloric acid (Eder: Piper and Carnegie, Amat. Photo. 1904, xl. 336, 397, and *ibid.* 1905, xli. 453, 473), this image, after washing, being developed by a solution of amidol (diaminophenol hydrochloride) in sodium sulphite. The chloro-chromate oxidises the image to a photochloride and the silver reduces the chloro-chromate, and the chromium compound

formed reinforces the image (C. W. Piper, Brit. J. Photo. 1907, liv. 3). In 1919, Lumière and Seyewetz proposed the use of an alkali chloro-chromate, preferably of ammonium, in place of the solution previously recommended, which is not alone a chloro-chromate, and they offer as an explanation of the changes which occur, that a double chromite of silver and alkali metal is formed together with silver chloride, which is reduced upon development with the amidol solution. On repetition a further amount of the double compound is formed and a less amount of silver chloride. The process can be continued until the silver left is very small (having been converted to the double compound), when no further increase is obtainable (*see* Brit. J. Photo. 1919, lxvi. 451 ; and for comments, R. E. Crowther, *ibid.* 709, and C. H. Bothamley, Photo. Journal, 1918, lviii. 52).

For intensification, Lumière and Seyewetz (Report Vth Int. Congress. Photo. 1910, 395) have proposed the use of benzoquinone and its sulphonic derivatives in the presence of a soluble bromide and chloride, by which means the silver image is converted to reddish-brown and yellowish-brown respectively—in acid solution, benzoquinone and benzoquinone sodium sulphonate act as reducers (*see* Compt. rend. 1910, cli. 616 ; J. Soc. Chem. Ind. 1228*a*). Wilsey (Brit. J. Photo. 1919, lxvi.) has systematised a process of intensification by redevelopment, in which the colour of the image is modified by stain produced by the oxidation of the developer (pyrogallol), the quantity of sulphite present being the determinant. In the case of a negative originally developed with pyrogallol when the stain is pronounced, a reduction can be effected by bleaching the image and redeveloping in a non stain-image producing developer as *metol-quinol.* Older methods of intensification are by treatment of the image with uranium ferrocyanide (Selle, 1865), mercuric bromide followed by potassium silver cyanide (Monckhoven, 1879), by mercuric iodide and sodium thiosulphate (Edwards, 1879), or in sodium sulphite (Lumière, 1900).

Reducing agents are varied in their effects, and these have been investigated as to their action by Huse and Nietz (Brit. J. Photo. 1916, lxiii. 580, and N. Deck, *ibid.* 391). The former authors adopt the following classification : Reducers which—

(*a*) Attack the highest densities principally, as ammonium persulphate (Lumière, 1898).

(*b*) Attack the lowest densities principally, as potassium ferricyanide and sodium thiosulphate (Farmer, 1883) ; and

(*c*) Proportional reducers, of which potassium permanganate and ammonium persulphate with sulphuric acid is an example (Deck, 1916).

Considerable theoretical and practical interest attaches to the use of ammonium persulphate as a reducing agent, and its action has been carefully studied (*see* Lumière and Seyewetz, Brit. J. Photo. 1921, lxviii. 124 ; Sheppard and Ballard, Photo. Journal, 1921, lxi. 450 ; Higson, *ibid.* 1921, lxi. 237 ; 1922, lxii. 89).

For a study of the action of reducing agents applied to prints, *see* L. A. Jones and C. E. Fawkes, Brit. J. Photo. 1921, lxviii. 276.

Positive or Print Making Processes.

The chief printing methods employ, as sensitive agents, compounds of silver, iron, and chromium, and the sensitive surface, which may be upon paper, glass, celluloid, or other suitable support, may be either one for 'print out' or for development.

Silver 'print out' contact surfaces.—The support is coated with an emulsion of silver chloride, with an organic salt of silver with citric or other organic acid, in gelatine (Abney, 1882) or collodion (Wharton Simpson, 1865), and generally the paper receives in the first instance a baryta gelatine substratum. This paper is exposed under the negative until the desired depth is produced, and is then washed to remove excess of soluble silver salt, and subsequently 'toned' with gold (Le Grey, 1847) to modify the colour. The 'toning' is effected by the deposition of gold, from a solution of gold trichloride in conjunction with, for example, either ammonium sulphocyanide (Meynier, 1863) or sodium phosphate. Many forms of 'toning' bath are used, but these cited are the most general. The prints are subsequently 'fixed' by immersion in a solution of sodium thiosulphate, which forms a soluble double silver salt, and afterwards well washed with water. The subsequent permanency of the print is largely affected by the care shown in fixation. In the so-called 'self-toning' paper the gold salt is added to the emulsion before the paper is coated, and the prints are 'toned' either on immersion direct in the fixing bath or by a preliminary water washing (or treatment in a solution of sodium chloride) followed by fixation. A considerable variety of colour from warm brown to purple may be obtained by the use of these emulsion papers, the self-toning collodion paper being probably the most pleasing and, undoubtedly, the most certain in its results. Collodion emulsion papers were first introduced commercially by Obernetter, of Munich, in 1867–68, who brought out gelatine emulsion papers in 1884. The first gelatine emulsion paper introduced in England was by the Ilford Company, in 1891. The nature of the toned image in printed-out silver halide emulsion papers has been discussed by Blake-Smith (*see* Brit. J. Photo. 1910, lvii. 173–176 ; *see* also F. Formstecher, Photo. Ind. 1922, 378, 403).

Silver 'development' surfaces for contact printing and enlarging.—The paper employed for this purpose are either plain silver bromide (first introduced by Mawdsley, 1874), bromochloride, or chloride (*Velox*, Baekeland, Nepera Company, 1890–1), the last furnishing the class to which the term 'gas light' was originally applied. These papers vary in sensitiveness, the chloride papers being the lowest. The different kinds of papers are distinguished by the character of the base, *i.e.* by the different classes of paper, when as in the main this form of support is used, by the 'surface' artificially given, and by the photographic range (contrast) and gradation properties of the sensitive coating (*see* B. T. J. Glover, Photo. Journal, 1922, lii. 132, and *discussion*). Certain emulsions (bromochloride) are made to yield brown-black images in lieu of the normal black. Exposure is made to artificial light for contact printing or to projected

images by means of daylight and artificial light enlarging systems, the sensitiveness of the surfaces varying considerably. For development a solution which will not stain gelatine or the paper fibre must be used, and the most generally employed agents are *metol-quinol* and *amidol*. Fixation is generally effected in an 'acid' fixing bath. For modification of the hue of the image in the developed print toning processes are used, the most usual being methods in which the image is sulphurised by treatment with a bath of sodium thiosulphate and common alum ('Hypo-alum' bath), by conversion to a halide—bromide or iodide—followed by a soluble sulphide, or by treatment of the silver image direct with a solution of 'potash liver of sulphur' — the polysulphide method. For recent work on sulphide toning, *see* E. R. Bullock (Brit. J. Photo. 1921, lxviii. 447).

Iron printing.—The sensitiveness of salts of iron—the reduction from the ferric to the ferrous state—was first utilised by Herschel in 1842 for the production of *ferro-prussiate* prints, and this method continues in use to the present day, being a very important method for copying of plans and tracings in line for industrial purposes. In the ferro-prussiate method suitable well-sized paper is coated with ferric-ammonium citrate and potassium ferricyanide and dried. Exposed under a black-and-white line tracing it yields afterwards upon immersion in plain water (or, better, a 0·2 p.c. solution of potassium ferricyanide, Eastman Kodak Report 1091, 1921), a negative image of ferrous ferricyanide (Turnbull's Blue) is produced, due to the reaction between the reduced iron salt and the alkali ferricyanide in the paper, the unexposed parts of the surface—those under the opaque parts of the tracing—washing out during development to white. This constitutes the blue print of commerce. Other important iron processes are the 'blue line on white ground' (Pellet, 1877), sepia (Arndt and Troost, 1894), and the ferrogallic (Riegel, Colas and others, 1880–1885), and these are principally used for plan printing.

A valuable application of the photo-sensitiveness of iron salts to the production of printing surfaces is that in which the change from the ferric to the ferrous state is utilised to produce an image in platinum (*see* Platinotype, Photo. Journal, 1883; Abney's translation of the Pizzighelli and Hubls work). This application was brought to fruition by Willis, who in 1873 introduced the first platinum process (*Platinotype* hot bath), since when the method has undergone several modifications. The original paper contained silver as well as platinum, but eventually the silver was eliminated, but its use has been revived (*Satista*, 1913), and in addition palladium has been used in lieu of platinum (*Palladiotype*, 1917). In the standard platinum process suitable well-sized paper is coated with a solution of potassium chloroplatinite and ferric oxalate and dried. The paper is exposed under the negative when the ferric oxalate is reduced to the ferrous state, the change being fairly rapid. Only a slight image is visible. The print is developed by flotation upon a solvent of ferrous oxalate—normal potassium oxalate or a mixture of that salt with monopotassium orthophosphate—when at the moment of its solution the ferrous oxalate reduces the platinum salt with which it is in contact to the metallic state, and this forms the image. The prints are then placed in dilute hydrochloric acid and subsequently washed and dried. By the introduction of a small quantity of a salt of mercury to the sensitising solution prints may be obtained of a sepia colour. The pictures are quite permanent.

The insolubilising action of ferric salts on gelatine is utilised in the so-called '*true to scale*' process of plan printing, where an undeveloped ferro-prussiate print is laid down for a few seconds upon a surface of a gelatine 'gel,' when the exposed parts—ferric salt—insolubilise the gelatine, and these parts will eventually take printers' ink from a roller passed over the surface, the unaffected portions rejecting the ink. The image is eventually transferred to paper or tracing cloth. The process is of considerable importance commercially (*see* R. B. Fishenden, Graph Process of Photo-Copying, Process Year Book, Penrose, London, 1910).

Carbon printing.—Mungo Ponton's experiment of 1839 (Soc. Arts, Edinburgh, May 19, 1839), whereby it was shown that sized paper which had been treated with a solution of potassium bichromate and dried, *darkened* upon exposure to light, has been continually developed, until, as the result, the chromium printing methods are of the greatest importance in all branches of pure and applied photography. Becquerel (1840) showed that the darkening of Ponton's paper was due to the sizing material present, and Fox Talbot (1852–53) demonstrated that gelatine in a mixture of that body with a bichromate became after exposure insoluble in hot water, and also less permeable. The work was carried further by Poitevin (1862). Poitevin's work culminated in the important process of carbon printing (*see* Chromium Printing, p. 245).

In the carbon process a sheet of paper coated with gelatine, an insoluble pigment, and potassium bichromate (carbon tissue), is exposed to light under a negative, when a change is produced in proportion to the amount of light action, which results in the gelatine being rendered insoluble in warm water (*see* Chromium printing, p. 245). The sheet is moistened and mounted, gelatine face down, upon a support of paper or other suitable material, which must be impermeable to air. The combination is placed in warm water, when, after a brief lapse of time, the paper backing to the gelatine is stripped away, and on laving the unchanged gelatine it washes away leaving a picture, the gradations of which are insoluble pigmented gelatine. From an ordinary negative the picture will be laterally reversed, and if such be of moment a reversed negative must be employed or the original print (single transfer) may be, if the support has been suitably prepared, transferred to another support (double transfer), when the second reversal compensates for the first. A considerable variety is possible by the process both in the colour of the pigment used and in the paper upon which the pigmented gelatine finally rests. Prints may be developed upon glass, porcelain, ivory, celluloid, metal, wood, and the results are permanent if the pigment used be so.

Through various modifications, *Carbograph* (Eng. Pat. 808, 24290, 1904); *Ozobrome* (Manley

Eng. Pat. 17007, 1905); *Carbro* (F. H. Farmer, F. Garon), there has been developed a modification of the carbon process in which exposure to light of the tissue is avoided. A sheet of tissue is soaked in a solution of potassium bromide, bichromate and ferricyanide is brought into contact with a developed and fixed bromide print which has been immersed in a solution of formaldehyde acidified with acetic and hydrochloric acids. After contact the tissue is separated and treated in the usual manner, or it may be developed on the bromide print, in which case the print is finally immersed in the sodium thiosulphate fixing bath and washed. In this process the silver acts as a catalyst.

If a sheet of gelatine-coated paper sensitised in an alkali bichromate be exposed to light, washed and dried, and again moistened with water, the print in a damp condition will take a varnish ink applied by a brush in accord with the varying insolubility produced by the light action. This is oil printing (Rawlings, 1904), and is an application of the principle of Poitevin's *collotype* process (1855) (*see* Photo-Mechanical Processes, p. 250). An extension of the ozobrome principle was first introduced by Welborne Piper in 1907, and termed *Bromoil* (*see* Photo. Journal, 1908, xlviii. 68). In this process a bromide print is treated with a solution which, whilst bleaching, produces insolubility of the gelatine proportional to the silver present. The precise composition of the bleacher varies, but Featherstone's combination—cupric sulphate, chrome alum, potassium bromide, and bichromate acidified with sulphuric acid—may be taken as an example. The print after bleaching is dried and again moistened. The damp print will take varnish ink in proportion to the gradations of the original print.

Both the oil and bromoil processes lend themselves to considerable modification from a pictorial aspect (*see* Bromoil and Oil Prints, Sinclair), and are important methods.

For the production of positives upon glass—transparencies—generally for lantern slides, plates coated with emulsions of either silver chloride, bromide, or bromochloride are used. These are all surfaces for development after exposure.

For practical details of the procedure in the use of different photo-printing materials the instructions issued by their makers will be found a reliable guide.

Colour Photography.

Processes of colour photography are divisible into two classes, viz. *additive* and *subtractive*. In the former method the hues in the representation are produced by colour synthesis, by addition, as the name implies, as in the Ives method, viz. by superimposition by suitable optical device, of three continuous tone positive images in coloured light, which are records of the colours of the object in terms of the primaries, red, green, and blue-violet, or, adopting the same principle by a single composite plate, 'screen plate,' which contains a uniformly distributed series of minute colour elements in hue corresponding to the primaries, and in quantity to satisfy the equation to white, and, in the latter—the subtractive method—by analysis when the hues are produced by the superimposition of coloured films representing the components, with white as the starting point. Upon this principle all methods of colour printing by means of photography depend. Thus it will be seen that in one method the colour image is built up by the addition of coloured light when the primaries red+green+blue-violet=white, and the function of photography is to regulate the quantity of each component required to yield any hue, and in the other method photography plays a similar part with the hues employed in the triad, *magenta* or −green, *yellow* or −blue, and *blue-green* or −red. Here the superimposition of the three, magenta+yellow+blue-green=black, and the particular quantity of each colour employed gives by subtraction from the original white surface—which is the starting point—the hue required to correspond to the original object. It will be seen that in both instances a neutral white is the starting point, and any variation will mean a difference in the final hues of the composite picture. The appearance, to take a simple case, of pictures produced by the so-called three-colour process of pigment printing is profoundly influenced by the final illumination of the completed picture, whether it be examined by normal daylight or by any ordinary artificial light. The principal colour processes in use to-day are the screen plate methods of Lumière (Eng. Pat. 22988, 25718, 1904; 9100, 1906) (introduced commercially, 1907), and Paget (1913) (Eng. Pat. Finlay 'Thames' 19652, 1906, and 4208, 1910). In the Lumière process a glass plate is coated with an adhesive varnish and then dusted with a mixture of starch grains dyed hues corresponding to the primaries red, blue-green, and violet, mixed in proportions to satisfy the equation to white. The grains are then crushed by rolling and the interstices are filled with a black powder. The plate is then varnished and afterwards coated thinly with a panchromatised gelatino-bromide of silver emulsion. Exposure in the camera is made through the back of the plate. After development the plate is treated with a solvent of silver (generally potassium permanganate with sulphuric acid), when the silver image is removed leaving the undeveloped halide. The plate is redeveloped and intensified (if necessary), washed and dried, and subsequently varnished for protection. In the Paget process (Photo. Journal, 1913, lxiii. 142) the screen and plate are separate. The screen plate—'taking screen'—is an assemblage of regularly placed small transparent elements in red, green, and blue-violet, formed by exposure under a suitable screen of a bichromated-colloid film, the insoluble units being subsequently dyed in colour solutions. As the pattern is a regular geometrical one, and the elements are in juxtaposition without any white interspace—as in the starch grain Lumière screen plate before the black filling is applied—the luminosity of the screen plate is relatively high. This plate is exposed in the camera in contact with a panchromatic dry plate, the light passing through the screen plate. From the developed plate a positive transparency is made which, when dry, is registered on a 'viewing screen' of the same pattern (but where the precise hues of

the screen elements are different) and the two are then permanently bound together to form the colour transparency. In both these methods it is necessary to use a yellow compensation filter on the lens to correct for the excess sensitiveness of the plate to the more refrangible end of the spectrum, and this screen must vary with the nature of the source of light employed.

Both processes yield transparencies, but the Paget process has been adapted for the production of colour prints. In this process, since the screen plate negative when made is separate from the taking screen, any number of positives may be made, and these when bound up with viewing screens will yield duplicate pictures, an advantage not possessed by the Lumière process. The most important processes utilising the subtractive principle are applications of the bichromated colloid process, as, for example, the carbon process and a modification of the carbon process, by Manners (Raydex) (Eng. Pat. 25646, 1910). For information and practical details of the latter, *see* Photo. Journal, 1919, lix. 238. In these processes coloured images produced from each of three negatives (made through three suitable red, green, and blue filters respectively) in blue, red, and yellow, are superimposed. In the Kodachrome (J. G. Capstaff) — two-colour — negatives are made through a red and a green filter. These silver images are then bleached in a solution which converts the image to silver bromide, in such a manner that the gelatine is hardened in proportion to the silver, so that when there is the most silver the greatest hardening takes place. The plates are fixed and washed and afterwards placed in dye baths, the red filter negative in a green dye bath and the green filter negative in a red dye bath, with the result that since the absorptions are inversely proportioned to the hardness a green *positive* and a red *positive* results. Afterwards, when the plates are dry, they are superimposed. Although there are deficiencies in the rendering the process will yield pleasing results of special subjects, as Portraiture, especially when they are viewed in a suitable artificial light. The method finds a useful field in certain forms of photography for surgical purposes, and in photo microscopy (*see* Sci. Amer. April 10, 1922; Brit. J. Photo. 1916, lxiii. Col. Supp. 30). The two-colour principle has been applied to kinematography, *see ante*, Capstaff's Process, Hist. Intro.

For details with respect to colour photography the undermentioned communications and works should be consulted: A Handbook of Photography in Colour, Bolas, Tallant and Senior, London, 1900; Optics of Trichromatic Photography, F. E. Ives (Traill-Taylor Memorial Lecture III.), Photo. Journal, 1900, xxv. 99; Photography of Colour, Hurter Memorial Lecture, Abney, J. Soc. Chem. Ind. 1901, xx.; Natural Colour Photography, König (translated by E. J. Wall), London, 1906; Screen Plate Processes of Colour Photography, G. E. Brown, Brit. J. Photo. Almanac, 1908, 557; Experimental Methods employed in the Examination of Screen Plates, Mees and Pledge, Photo. Journal, 1910, l. 197, and Brit. J. Photo. 1910, lvii., Col. Supp. 45, 53 (a most valuable paper on the theoretical and practical requirements of the screen plate); Three-Colour Photography, von Hubl (translated by O. Klein), London, 1915; Colour Photography, C. E. K. Mees (Photo-Miniature Series, No. 183), 1921.

Photo-Mechanical Processes.

In addition to the processes of pure photography in which the results are obtained by light action aided by subsequent chemical operations, there are other methods of photographic picture making. These constitute a group by themselves of considerable industrial importance, differing from the purely photographic methods in so far that they yield their results partly by chemical and partly by mechanical means. Photography is utilised in the production of surfaces from which prints are afterwards obtained in printer's ink. Such processes employ the different forms of printing press, and to them the term *photo-mechanical* is applied. They are used for the production of transcripts of drawings and paintings of different kinds and for the multiplication of copies of photographs of natural objects. By far the greater portion of the illustrated books and periodicals now made utilise photography in this manner. The processes are divided into three groups, *intaglio*, *surface*, and *relief*, according to the form of the ink-bearing medium. The term 'surface' is for convenience generally employed (although it is not strictly correct), and it is the function of this photographically prepared surface to hold the ink (afterwards to be transferred to paper, and also now in many cases to fabric), distributed in such order and quantity as will render the various tones of the picture. For a simple understanding of the differences in the three groups, consider a plane surface as the starting-point. Then, in an intaglio process, the ink-holding portions are sunk below that surface, as, for example, in a steel engraving—in a *surface* process the ink-bearing parts and those which do not bear ink are in the plane of that surface after the manner of a picture upon a 'lithographic' stone, whilst in a *relief* process certain portions of the original surface have been removed, forming depressions, leaving other portions which are to bear ink standing in relief, the simplest illustration of this form of surface being an ordinary woodcut. It will be seen that a relief process—so far as the finished result is concerned—is the exact reverse of an intaglio process. Methods coming under these two designations yield printing media which fulfil their purposes by utilising purely mechanical principles. This is not so, however, with surface processes, for the physical state of the surface produced by chemical change largely determines their working.

The following list gives the typical and more important processes according to their character in the groups already given:—

Intaglio.

Intaglio, line and half-tone (invert half-tone), flat or cylindrical surface.
Talbot-Klic photogravure (gradated tone), flat surface.
Rotary photogravure—cylindrical surface.
Woodburytype.

Surface.

Photo-lithography.
Photo-zincography.
Photoalgraphy.
Collotype.

Relief.

Line block processes.
Tone „ „
Colour processes (tri- and multi-colour methods) may be employed in all the groups; they have been most used in connection with relief processes, but an increasing amount of colour printing on a three-colour basis is being done by surface printing.
Combination processes between methods in the same group or between those in more than one group, as for example, collotype and lithography, lithography and tone block processes, lithography and photogravure.

Negatives required for photo-mechanical methods are made by means of wet collodion, collodion emulsion, and by dry plates. The first-named process is the one principally used for the majority of purposes, for the reason that it is the most economical and gives easily the kind of negative required. When, however, subjects in colour are to be rendered either in monochrome or in colour, the choice lies between the two latter methods. The modern panchromatic dry plate of suitable type has, however, almost replaced collodion emulsion and will probably do so entirely, excepting for special purposes.

The second step is the making of the surface. Practically the whole of the photo-mechanical processes are based upon the changes which occur when albumen, gelatin and its degradation product gelatose (of which the substance 'fish glue' is the most important example) are exposed to light in conjunction with alkali bichromates. Generally the insoluble bodies so produced are employed as protective agents or 'resists' upon the surface of a metal against the action of some solvent of that metal (intaglio and relief block processes), or they may be used in the production of an ink image to be applied to stone or metal as an intermediary (lithography, zincography, algraphy), or to paper as finality (collotype).

Chromium Printing.

If gelatin be placed in a cold solution of an alkali bichromate, the body swells, behaving in the same manner as when immersed in water. If the swollen mass be dried and kept in the dark without special precaution, no alteration takes place which materially affects the properties of the gelatin, except after some hours. The period of immunity from change largely depends upon the temperature and the amount of moisture present in the mass. In warm and especially during damp weather, a material change may take place in 12 hours, and the result of that change is that the gelatin has reduced some of the chromium salt, the mass has lost its yellow colour, becoming dull orange, its absorption capacity for water, and the increase in volume consequent, is lowered, and the temperature at which the body when swollen in water passes from the 'gel' to the liquid state is raised. As time goes on, the changes in the normally dry chromated mass increases, with the result that the gelatin almost wholly refuses to absorb water, and it will not dissolve at increased temperature — the gelatin has become insoluble.

If the bichromated gelatin be kept in a cool and dry atmosphere it will remain practically in its original state for several days; and with complete desiccation, no change of moment can be observed after many weeks' storage.

The change in appearance and behaviour thus indicated proceeds with great rapidity in the presence of light, provided that the bichromated gelatin is ordinarily dry. In the moist state the alteration is extremely slow. Gelatin may therefore be said to form in conjunction with an alkali bichromate a mixture sensitive to light. What is true of gelatin holds good for many other substances; for example, to its parent *collagen* and to its primary degradation product *gelatose*, to albumen, gum arabic, and to starch. All these substances reduce alkali bichromates in the dark, but more rapidly in the presence of light, and yield residues which are insoluble in hot water. Many bodies akin to those instanced—gelatin peptone is important in this respect—reduce bichromates but do not yield insoluble products. The feature which it is important to notice is the change in solubility in water and the properties which accompany this change, for upon these the interest and value to the photographer and to the photo-mechanical worker depend.

Intaglio Processes.

Woodburytype.—This process was the invention of the late W. B. Woodbury, and is especially interesting in that it forms a bridge between the purely photographic and the photo-mechanical process. The printing plate consists of a sheet of lead which is impressed with a series of cavities the variation in depth of which corresponds to the light and shade of the different portions of the picture it represents. A carbon print (see *Carbon Printing*, p. 242) is a picture produced in insoluble gelatin which holds in suspension finely-divided carbon or other pigmentary matter. The picture tones are represented by various thicknesses of insoluble gelatin, and such tones show a sensible amount of relief. By the use of a specially thick film of gelatin the amount of relief may be increased, and if such a film be developed upon a film of collodion there is obtained what is known as the Woodbury 'relief,' which is merely a carbon picture held upon a thin film of textureless collodion instead of upon the fibrous paper, as is customary with a carbon print. When the film is dry, there remain varying thicknesses of hard gelatin, and it so happens that this is capable of resisting considerable pressure. If the relief be laid upon the bed of a hydraulic press and a sheet of pure lead be put above it and pressure applied (the precaution being taken to prevent the lead flowing laterally), a perfect mould will be made of the relief, and

without damage to the gelatin picture. The gelatin relief can be readily removed and the result will be an intaglio copy in lead. If, when the carbon print has been removed, the space left is filled up with a solution of gelatin containing pigment and this gelatin is allowed to set, to all intents and purposes, the condition is the same as it was in the first instance, except that one filling material was dry gelatin, and the other is wet gelatin. If we allow this gelatin to set, attaching to it previously some substance by which it can eventually be withdrawn, a print will be produced similar to the one used for making the mould. The latter was a carbon print produced by the agency of light, and now from a leaden intaglio plate or mould a similar carbon print is obtained, purely by mechanical means and without light action. When once the leaden relief is produced, prints are readily made merely by pouring into the mould a solution of gelatin containing pigment suitably adjusted as to quantity, placing on the top a sheet of paper, and applying even pressure above. The excess of gelatin is squeezed out at once, that remaining in the mould sets in a short time, and upon lifting the paper away the gelatin will come with it. A Woodbury print is then simply a carbon print produced mechanically and consists, as does the carbon print, of a layer of gelatin of varying thickness, the only other difference being that in the case of the light-produced carbon picture the gelatin is insoluble, and in the mechanically-produced carbon print it is not. This process is probably the most perfect of all the photo-mechanical processes, so far as the rendering of tone is concerned. Very great variety can be obtained, the colour depending upon the pigment used with the gelatin. The process *Stannotype*, also due to Woodbury, was a modification of this method designed to avoid the necessity for hydraulic pressure in the production of a mould. The plate was formed from a negative carbon relief in gelatin faced with tin foil forced into contact with the relief by rubber roller pressure. These processes are no longer employed, but they remain of great theoretical and technical interest.

Photogravure.—A photogravure plate is a sheet of copper bearing an image formed by means of cavities of different depths, which represent the gradations of the picture. These cavities are filled with an ink composed of linseed varnish and a pigment (for example, lamp black), which ink is afterwards transferred to paper by means of pressure in the copper plate printing press. The process most generally used is that known as the Talbot-Klic.

Any drawing in line or gradated tones in monochrome or colour or any photograph of a natural object may be rendered by this process. Whatever be the original, a negative must first be prepared of the desired size, and from this negative a positive transparency is made which should be laterally reversed. If the subject be a line drawing the positive may be produced by means of a gelatine-bromide dry plate or by wet collodion. If the negative represents a drawing in gradated tones—for example, a wash drawing, an ordinary water colour or an oil painting or a photograph of a natural subject—it should be unreversed and from it a positive transparency is made by the carbon process, which produces the reversal required without further operation. The method gives probably the best rendering of tone, but in commercial work a reversed positive is frequently made by the dry-plate process. The latter plan has the advantage that the size of the positive may be varied from that of the original negative which is frequently required.

The process of photogravure consists in forming upon the surface of a sheet of copper, on which there is deposited a fine dust of bitumen (or other suitable resin), an insoluble gelatin image. The plate bearing the dry gelatin image is placed in a solution of ferric chloride which is absorbed, when swelling and penetration of the film takes place—the solution eventually reaches and then etches the metal. This process may be termed ‘through’ etching. The various thicknesses of the gelatin which form the gradations of the image determine the commencement of the action of the mordant, so that in a given time different amounts of etching are produced, which vary directly with the tones of the picture. When the etching is completed the gelatin is removed, the plate cleaned, and it is then ready for proofing in the press.

This gelatin image governing the etching is a negative image, and is the ‘resist.’ It is produced by the carbon process, in the ordinary manner of the carbon printer, by developing on the metal a tissue exposed under the reversed positive from the negative of the subject. The dust coating is termed the ‘grain.’ Its function is to protect minute areas of the surface of the metal from the attack of the mordant. A patch of uniform tone of appreciable size is not represented by a smooth etched cavity corresponding to that patch of tone, but is covered with a number of small dots, undistinguishable as separate elements by the unaided eye.

Failing this condition—however it may be produced—in the plate, the printing ink could not be held prior to transfer to the paper which forms the final support of the image.

The ‘grain’ is produced by exposing the plate in a box which contains suspended in its atmosphere very finely divided bitumen or colophony. The ‘graining box’ must be of considerable volume and large in horizontal sectional dimensions in proportion to the dimensions of the copper plate, in order to enable uniform graining to be obtained over the whole area of the surface. When the amount of dust deposited is sufficient the plate is removed and gently heated, when the grains soften and adhere firmly to the metal. The success of the process is largely dependent upon suitable graining of the plate.

The copper used for plate making must be pure, hard, and homogeneous, the surface planished and highly polished. The carbon tissue is preferably one containing only a small quantity of pigment in order that the colour of the metal may be seen through the film. The correct exposure for the tissue under the positive should be ascertained by trial exposure, developing such trials upon opal glass.

The solution of ferric chloride (saturated with ferric hydrate or cuprous chloride) employed as mordant is prepared by dissolving the salt in

water to that degree of saturation which registers 45°Baume at 16°C., and from this solution others are prepared by dilution to densities 33°, 35°, 38°, 40° and 43°B. The more concentrated the mordant the slower the rate of penetration. A very concentrated solution may not in reasonable time penetrate even the thinnest portions of the resist. If such fails, the solution is poured away and a weaker one employed. When the ferric chloride reaches the copper, a darkening takes place showing that the etching has started. Such action will continue to other and lighter tones as the mordant penetrates, and to secure this end the weaker solutions are used successively until even the thickest layer of gelatine is penetrated. Errors in timing or in the use of unsuitable solution lead to faulty rendering of the scale of gradation.

When the etching is completed the metal plate is at once placed in a solution of caustic soda, which arrests the action of the mordant. The plate is washed in water, scrubbed with a soft brush, brushed with dilute sulphuric acid, potassium cyanide solution or a mixture of acetic acid, common salt and water, and afterwards with turpentine to remove the 'grain,' again washed and dried.

The plate is printed after the manner of a copper-plate etching, and in photogravure much of the success is due to skilful treatment in this operation. If only a few copies are required the plate may be printed at once; but for any quantity it is necessary that the surface be 'steel faced,' in order to protect the image from wear in the printing process.

Usually photogravure plates require considerable modification at the hands of a skilful engraver by means of the burnisher and roulette, and by a process of selective etching for which the plate is afterwards specially prepared.

Invert Half-Tone Intaglio Printing.

A form of intaglio printing consists in adapting the ruled screen half-tone principle (see *Tone block processes*). A screen positive is made from an ordinary negative (continuous tone) and from this positive a print is made upon copper by the enameline process (see *Enameline printing*). This print forms the resist. The plate is afterwards etched in a solution of ferric chloride, and the etched metal is printed in the copper plate printing press. The gradations of light and shade are rendered by dots of various sizes (the number per unit area depending on the ruling of the screen employed when making the screen positive), as in the half-tone block process, but each etched cavity is the same depth. The same process with certain modifications is also used in the reproduction of subjects in pure line.

Rotary Printing of Invert Half Tone.

Instead of using a flat surface of copper, a cylinder of the metal may be employed. This offers considerable advantages, inasmuch as it permits of the adoption of the rotary method of printing with the consequent gain in speed of output and in certain other directions the process is useful, as, for example, in the illustration of the less expensive forms of printed matter, newspapers, periodicals and the like. Special devices are used by which the sensitive coating (fish glue and an alkali bichromate) is applied to the roller and a flexible film form of half-tone screen positive is caused to adhere to the cylinder by a suitable fluid medium—as, for example, mineral oil—which does not affect the sensitive coating. After exposure to light, the image is developed, dried, and 'enamelled' by heat. Those portions of the roller not covered with an image are now varnished by a protecting medium, and afterwards the roller is treated with the mordant. The printing of such cylinders differs from that employed with any other photo-mechanical process. The machine employed consists of a large cylinder or bowl covered with partially vulcanised rubber or upon which is stretched a felt blanket, and over this is fed the paper from an endless reel. The engraved roller is supported in contact with the printing paper, the pressure between the two being variable at will. The inking is usually effected by supplying the printing colour to the roller as it revolves from a 'furnishing' roller which revolves in a trough containing the printing ink. The excess of colour is removed by means of a thin steel knife-edge blade termed the 'doctor,' which is caused to press upon the roller with sufficient pressure to remove the superfluous ink from the surface. The colour remains in the etched hollows. The surface-clean portion of the roller next comes in contact with the printing paper, when transference of the colour from the cavities takes place. It will be seen that the steel 'doctor' with its perfectly smooth edge replaces the hand wiping of the copper plate printer. Perfect fitting of the two surfaces, the 'doctor' and the cylinder, is necessary. The ink used must be much thinner in consistency and of a different character to that employed for ordinary copper-plate printing or the surface of the roller cannot be made clean by the 'doctor.' This method of inking does not offer the same opportunity for modification as that used by the ordinary copper-plate printer, whose craft is extremely personal, offering abundant field for the exercise of taste. In consequence, excellence of result in all 'doctor' or mechanically wiped intaglio printing depends largely upon the quality of the engraving work.

Rotary Printing of Photogravure.

Rotary photogravure.—The method of printing ordinary photogravure plates does not lend itself to speed of production, and the result is that the prints are relatively costly, especially for large sizes. Photogravure plates, as in the case of ordinary copper or steel intaglio etchings, can be printed with success upon special flat-bed printing machines, when the wiping of the plates is effected by means of a 'doctor' or by a travelling band of paper. It is, however, found in the case of the delicate photogravure plate that considerable wear takes place. In 1895 the rotary principle was applied to photogravure in the 'Rembrandt' process. For a number of years the method of working was kept a close secret, but the principles employed are now known and the process is employed

commercially and in the illustration of newspapers and magazines. The 'invert half-tone' process should not be regarded as the same as photogravure, for the reason that 'through etching' is necessary to give the characteristic effect of the latter process, the etched cavities of the rotary photogravure plate, unlike 'invert half tone,' varying in depth, an important element in producing the beautiful effects of the method. The essential difference between 'rotary gravure' and Talbot Klic photogravure is that for the bitumen grain in the latter process is substituted a network of lines. A piece of specially prepared carbon tissue is exposed to light behind a laterally transposed positive transparency and in addition an exposure is made behind a special type of ruled screen (Fig. 2). The exposed tissue is mounted and developed upon a cylinder upon which copper has been electrolytically deposited between one-eighth and a quarter of an inch in thickness and ground to a true surface. The etching is carried out in the same manner as in the Talbot Klic process; the roller so prepared is then printed after the manner previously outlined.

The quality of result obtained by the rotary process adopted by the best firms is very high, the rollers being singularly free from obvious evidences of the use of the hand engraver's tools. This is largely due to the perfection of the method itself and to the attention paid to the making of the negative and positive and to their skilled retouching. It is anticipated that the near future will see a wide extension of the use of this process, which, in the simplicity of the printing machinery employed, has considerable advantages over letterpress printing or lithography. The wide range in the character of the results is remarkable. Under suitable conditions illustrations comparable with mezzotint quality can be produced, and it has been shown that it is also possible, with inexpensive paper and ink, to make excellent prints which could not be produced by other printing processes. Rotary gravure has been used for newspaper illustrations, produced at the ordinary speeds of newspaper printing; it is usual in such cases to etch the type matter on the same cylinder as the pictures.



Fig. 2.

Photogravure in colour.—Prints in colours are produced by applying colour inks to the engraved plates, which are etched more deeply than for monochrome. The coloured inks are applied to the plates by sponges or by dabbers of different sizes and for small details by stumps, and the plates are wiped in the usual way. The transfer of the ink to the paper is completed at one operation. The process is naturally slow, and the results, though often very fine, are costly.

The rotary principle has been applied to the production of photogravure prints in colours with success. Combinations of rotary photogravure with lithography, and especially offset lithography, are also employed for colour work.

Flat plates prepared exactly in the same way as for rotary printing are now printed successfully both in monochrome and colour, using a doctor wipe on machines of the die press type.

Surface Processes.

Photo-lithography.—A lithographic print is a picture in varnish-ink produced from the surface of a calcareous stone. Ordinarily, the design upon the stone which produces its selective attraction for the ink upon the inking roller is produced by drawing upon the surface with a fatty medium, but the original design may be copied by photography and transferred to the stone from which prints may afterwards be produced. Such copies are photolithographs. Any drawing in pure line or in continuous tone may be reproduced in this way. Two methods are adopted—direct and transfer. The negatives most suitable for the production of prints in line are made by the collodion process, but this special photomechanical or 'process' dry plates are excellent for the purpose if the original drawing be suitable for *small* work. The negatives must be reversed. For the 'direct' process the surface of a well-polished lithographic stone is warmed and is then coated evenly with a solution of fish glue (or albumen) and ammonium bichromate in water. The film should be thin. After drying the stone is ready for exposure. For *small* subjects an ordinary glass negative may be used, which is pressed into contact in a specially constructed frame with plate glass front. It is more satisfactory, and is indeed necessary with large sizes, to use thin film negatives, which may be arranged on the plate-glass bed of the frame over which the stone is then placed. To avoid the cost and inconvenience of larger frames, the film negatives may be gently 'squeegeed' into contact with the sensitive surface, using as a cementing medium a solution of mineral oil in naphtha, all traces of which may afterwards be removed by treatment of the surface by naphtha, followed by benzene, without damage to the exposed sensitive coating. The film negatives which should be *collodion* films, strengthened before removal from the glass plate by coating with a solution of rubber in benzene have no 'spring' and adhere easily.

After suitable exposure the surface of the stone is coated by means of a composition roller with a thin film of lithographic *transfer* ink thinned with turpentine or naphtha. After evaporation of the solvent the surface of the stone is flooded with water. On gently rubbing with a tuft of cotton wool the unaffected portions of the coating wash away carrying their covering of ink, and there remains an image of the insoluble fish glue bearing upon its surface the coating of the fatty transfer ink. The stone is then covered with a solution of gum arabic in water which is allowed to dry, after which it is *preferably* allowed to stand for a few hours, when it is ready for the lithographic printer, to be 'rolled up' with lithographic printing ink, dusted with resin which adheres to the ink image, etched with very dilute nitric acid, 'washed out' with turpentine and again rolled up with ink, when an impression may be taken in the lithographic press. Corrections and additional matter may easily be put upon the stone. The effect of the treatment to which

the stone has been subjected has been to form upon its surface an image in fatty salts of calcium. This is the usually accepted view, though it is doubtful whether this be entirely correct, whether the fatty matter does actually penetrate the insoluble film. The negative effects of the gum and acid in the unprotected parts of the stone—the non-image parts—are quite sufficient in themselves to produce an image on rolling up, because the ink takes to the image parts only, and not to the bare stone. If, however, the fatty matter does penetrate, fatty compounds of calcium are assumed to be formed, which is the generally accepted view in case when a fatty drawing is made direct or transferred to the plain clean stone as in many kinds of lithography. This image rejects water whilst the unaffected portions of the stone hold water. If while the surface is in a damp condition, varnish ink (pigment and linseed varnish) be applied, such ink will be deposited upon the image but not upon the damp portions of the stone where no fatty salt has been formed. This, in brief, is the leading principle in the production of an image by lithography. If paper be laid down upon the inked surface and pressure be applied, the ink is transferred to the paper, and the cycle of operations—damping, rolling, and printing—is repeated for subsequent copies.

This form of the process—direct printing on stone—is now principally of historical interest only, for in recent years litho stones have been largely replaced by thin zinc or aluminium plates, the surfaces of which are mechanically grained so that moisture may be retained and the greasy image firmly held. The great advantage of the use of metal is that the plates may be attached to rotary machines and thus increased production secured. In modern practice, negatives are printed direct on to machine plates, and the use of special vacuum printing frames enables the negatives to be duplicated in accurate register. By means of ' step and repeat ' machines, small subjects, such as lables, may be duplicated many times in correct position. The introduction of ' offset ' printing, wherein the ink is transferred from the printing plate to rubber, and from thence to paper, has enabled a great variety of new effects to be obtained at a low cost.

In the reproduction of type pages by photo-lithography a process has been used in which a negative is made on glass coated with a bichromated colloid; this is exposed to light in contact with the printed page, the light passing through the sensitive coating. The difference in the amount of light reflected back into the sensitive film causes the portions corresponding to the white portion of the paper to be rendered insoluble. After washing out, the insoluble film is stained with a dye and printed from in the usual manner.

If the original picture to be copied be in continuous tone, a ruled screen negative (*see Half-tone screen process*) is made, in which the full range of tonal gradation is used, described as a ' high light ' negative; this is used for printing upon the coated surface as described. This process requires considerable attention to details, especially in the selection of the surface and preparation of the negative, and finds its most useful application, not for monochrome, where the copies tend to show a flat scale of gradation, but for photo-chromo-lithography, in which a number of separate impressions in different coloured inks from different plates are superimposed, after the manner of the chromo-lithographer, for the production of pictures in colour from an original in colour.

In the transfer process a sheet of paper coated with gelatin (photolitho paper) is immersed for a few minutes in a 3 p.c. solution of potassium bichromate and afterwards dried in the dark, preferably in a freely moving current of air, in order to ensure rapid drying. It is then printed under a negative (unreversed) of the subject in line to be copied, care being taken to ensure perfect contact of paper and negative, and to avoid undue exposure to light, which causes increase in the thickness of the lines forming the image. After exposure, the sheet is placed on a flat surface and coated with ' transfer ' ink by means of a roller, avoiding excess. After evaporation of the solvent, the inked sheet is placed in water at 16° (approx.), where it is allowed to remain for a few minutes, when it is removed and placed face upwards upon a sheet of glass. The unexposed portions of the gelatin absorb water and swell, but this effect only takes place in the exposed parts to a very slight extent. Upon gently rubbing with a tuft of moist cotton wool, the ink will leave the swollen parts but adhere to the exposed portions. When this process of development is complete there will remain an image of insolubilised gelatin bearing a coating of ink, upon a ground of clean gelatin. This picture—the transfer—is then allowed to dry. It is afterwards damped, when the ink image may be transferred to stone or metal by the usual procedure.

Transfers produced from screen negatives for the production of subjects in continuous tone are only satisfactory when the negatives are made with coarse screen, owing to the tendency of the dots to spread, first in the exposure, afterwards in the inking, but principally in the transfer process.

One advantage of the direct over the transfer process lies in the avoidance of stretch, a necessary consequence with paper. Direct work on metal plates now largely replaces ' transfer ' work. This avoids the stretch and sharper results are produced. The plates may be printed from directly, or ordinary transfers may be taken on suitable paper and retransferred to metal plates or stone. In this way many transfers of the one plate can be laid down on a large plate so as to multiply the copies produced at one impression on the machine or press.

Photo-lithography in tone.—A process for the production of continuous tone subjects—nature negatives and copies of drawings—depends upon the fact that if the thickness of the gelatin coating upon a gelatin ' transfer ' paper be increased and contain in addition to the bichromate other substances as, for example, sodium chloride and potassium ferricyanide, the film, after exposure under an ordinary negative and soaking in water, will swell and reticulate in varying degree according to the amount of light action produced under the different portions of the negative. This reticulation of the surface of the transfer means that

the film will no longer be continuous in one plane, but broken up into 'grain,' and if ink, transfer ink, for example, be applied, it will adhere to the image in isolated masses of varying size, which are capable of producing the illusion of shading. The 'grain' can be varied to suit the subject; and the finer the detail to be rendered, the finer the 'grain' should be. The ink image is eventually transferred to stone (*v.* also *Collotype*). From the finished stone, transfers can be taken which can be utilised in the production of a series of new stones, which after careful modification by hand can be employed in the production of pictures in colours by chromo lithography. Photo-chromo work is also produced in five or more printings on a three-colour basis, supplemented by hand correction, especially in conjunction with offset printing, using a variety of methods to obtain the necessary grain.

Photozincography and photoalgraphy.—These are processes in which zinc and aluminium are used in place of the lithographic stone as the printing surface, and the methods employed are similar to those described. 'Photozincography' is sometimes applied to relief line etching. The general term 'photo-lithography' is used increasingly for work on metal plate. Direct work on plates for direct printing or retransferring has largely superseded paper transfers.

Collotype.—A collotype print is a picture in varnish ink obtained from the surface of chromated gelatin which is supported upon a rigid body, generally glass. Such a surface is produced by exposing the bichromated gelatin-coated glass under a negative and afterwards removing the unaltered chromium salt by washing in cold water, when the film is dried spontaneously. If the film be afterwards moistened with an aqueous solution of glycerol and ammonia, this solution will be absorbed, and the gelatin will swell slightly. If the excess of this 'damping' solution be removed and a charged roller be passed over the surface, the ink from the roller will be taken by the different parts of the film proportionally to the amount of light action which has taken place during the exposure under the negative, and this ink may be readily transferred to paper by simple pressure. By this process it is therefore possible to render automatically by purely chemico-physical means the gradations of light and shade in the negative in such a form as to be utilisable in the printing press. It is interesting to compare this process with Woodburytype, where the translation is mechanical, and with the half-tone block process, where it is produced by optical means.

Provided that a suitable negative be made, any subject can be rendered in collotype. The plates may be printed in the press, where the manipulations are wholly by hand, or in the machine, where the damping is done by hand at frequent intervals and the inking and printing are mechanical. The rate of printing of the best class of collotype is slow. The process is valuable for the reason that it is capable of yielding pictures the gradations of which are faithful to the negative and, as compared with the half-tone block process, without the disturbing effect of the regular dot formation. The variety of printing paper that can be used is considerable, and because of this fact the process has additional value.

For the preparation of the printing surface a sheet of plate glass, $\frac{3}{8}$ to $\frac{5}{8}$ inch in thickness, is finely ground upon its surface and is then flowed over with a solution of an alkaline silicate and white of egg, or in modern practice with a solution of an alkaline silicate, chrome alum and gelatin. After evaporation of the water, the plate is heated to about 60°. It is then cooled and washed in cold water and afterwards allowed to dry. This process is termed 'substratuming,' and its purpose is to cause a deposit of silica upon the glass. The deposit, in addition to the roughness of the glass, causes the subsequent film of gelatin to adhere strongly. This device is necessary owing to the mechanical strain upon the film caused by the operations of rolling and printing.

The sensitive film is produced by coating the plate with a solution of gelatin and alkali bichromate in water. The gelatin used must be of high grade and of medium 'hardness' and free from fatty matter. The prepared glass is warmed and levelled, and the requisite quantity of the solution is poured upon the surface and spread in any convenient manner. Drying must take place by evaporation at an elevated temperature—there is no intermediate setting to form a 'gel.' Upon correct conduct of this drying the success of the plate maker largely depends. To this end, the plate rests upon levelling screws in a drying oven, which is a box—generally constructed of wood—large in volume, and kept at the suitable temperature by means of a steam or hot-water radiator. Gas or oil heating may be used, provided that care is taken to prevent the products of combustion entering the chamber containing the plates. The construction of the oven must be such that there is no internal vibration and that there are no 'draughts.' Failing these conditions the film will dry with an uneven surface—a fatal defect. The top of the box must be covered with a fabric which will permit the passage of the water vapour from the plates out of the oven.

The oven temperature, varied between 40°–60°, influences the character of the film. When the film of gelatin is dry the oven is allowed to cool, and afterwards the plates are removed and are kept in the dark. The films will remain in good condition for 1–2 days, depending upon the atmospheric surroundings. If, however, storage takes place in an artificially dried atmosphere, as in a storage box containing a tray full of calcium chloride, the plates may be kept 5–6 days. Deterioration is due to spontaneous insolubilisation of the film. For collotypes, laterally transposed negatives are required. In practice, the plates may be printed (exposed), in the case of small pictures, from glass-plate negatives. More perfect contact between the surfaces is obtained by printing from flexible film negatives prepared for the purpose, which are laid upon the plate glass bed of the printing frame. By means of thin tin foil the negatives are masked at the margins to show only the amount of subject required. Exposure takes place in the ordinary way, but the frames have usually no backs, so that the under side of the film may be examined in order to observe

the progress of printing. The film darkens in proportion to the duration of exposure. Usually, the printer determines the correct amount required by judgment. When the plate has been exposed sufficiently, it is removed, and is then quickly and evenly immersed in water or it may be flooded. Washing continues until the free bichromate is removed, when the film will be practically without colour. It is then dried. Examination of the plate before drying, at this stage, shows that the image is in slight relief and that it is reticulated. A certain amount of 'grain' is required to ensure successful printing at the press, but such 'grain' should not be obvious to the unaided eye. The following conditions influence the character of the 'grain'; kind of gelatin; thickness of film; proportion of bichromate present; the particular alkali bichromate used; drying temperature; length of time the plates have been kept previous to exposing under the negative; the after treatment of the exposed and washed-out plates and the addition of special salts, as, for example, calcium chloride and potassium ferricyanide (*v.* also *Photo-lithography in half-tone*). For special purposes—for example, amongst others, the means of making transfers for half-tone lithography—plates are sometimes prepared to give a coarse 'grain' by the addition of the last two named substances, although this is not the only method, nor are they when used the sole determinants.

Printing.—The plate during printing must be in a damp condition. This may be secured by simple water damping, but when water alone is used, frequent application is necessary, which makes print making a slow process, and moreover is useable only for hand-press printing. Generally water containing a hygroscopic substance as, for instance, glycerol or calcium chloride, is used with addition of ammonia which softens the film. When the film is in a sufficiently moist condition, the superfluous solution is removed, the plate is ready for the press or machine. During printing, the damping solution is re-applied to the ink-free film as required from time to time.

The printing inks used must be specially prepared from *finely ground* lakes and other suitable pigments. No body of a gritty character should be used. The medium should be linseed varnish of high quality; non-drying oils and fatty matter must be avoided. As the film of ink allowable upon the image is very thin, the medium should be 'loaded' with pigment and in consequence collotype inks of high grade are very stiff. For use, the printer employs as reducing agent when required 'middle' and 'thin' linseed varnish.

The rollers used are leather, 'nap' and smooth, and also gelatin composition. A nap roller, charged with stiff ink, is applied to the plate and with frequent rolling the dark and middle tones are produced, after which the smooth leather or composition roller, covered with thinner ink, is used for the more delicate gradations. After inking, the ink from the plate is transferred to the paper (or somctimes a fabric) by pressure. The paper used must be of absorbent nature and of medium hardness. Given these conditions, considerable variety is possible.

Collotype in colour.—If the grain of a collotype plate is fairly pronounced, it is possible to transfer a printed image to a lithographic stone, and by such means beautiful colour work has been done. For such productions, plates are specially prepared from negatives which have received considerable modification (by retouching and masking), so that the gradations are made to coincide as far as possible with the amount of particular printing colours required for any region, when superimposition of the different printings will yield the hue required. The stones forming the series for any picture require considerable correction at the hands of a competent lithographic draughtsman, and it is largely owing to his skill that good results are due; hence the process is costly.

Another method is to print from several plates in separate colours from different negatives which have been modified by hand work, superimposing the coloured impressions. The most perfect method where collotype is used is to produce one or two of the necessary printings from collotype plates, generally in neutral tints, and to complete the picture by hand-drawn lithographic stones. This process yields in skilful hands beautiful results. In one proprietary process only the light colours are printed as transfers to stone, the remainder are collotype. Collotype has been employed also in the three-colour process—for which it is, *ab initio*, unsuitable.

Collotype pure and simple, by reason of the fact that a printing surface of damp gelatin is used—which is liable to be affected by changes in the hygrometric condition of the atmosphere—is a process difficult to work so as to produce very uniform results. Whilst slight variations are not serious in monochrome printing they become so when colour work is attempted. For this reason, mainly, collotype in colours is difficult and in consequence the products are relatively costly.

Relief Processes.

In the pictorial representation of any object the form is rendered either by pure line, as in simple pen and ink drawing where the lines may be assumed, for simplicity's sake, to be all of uniform depth of colour, or by patches of pigment of varying intensity, either in monochrome or colours, as in a wash drawing or in an oil painting. The former may be termed 'broken' tone and the latter, 'closed' or 'continuous' tone. A third division is formed by a combination of both these methods—a picture may be formed of washes of pigment in conjunction with pure line. An impression in printer's ink from a forme of type matter (the page of this book, for instance) is an example of broken tones: the transition from ink to paper is abrupt. A photographic portrait is in continuous tone, there is no discontinuity in the shading by which the form of the person and surroundings is represented.

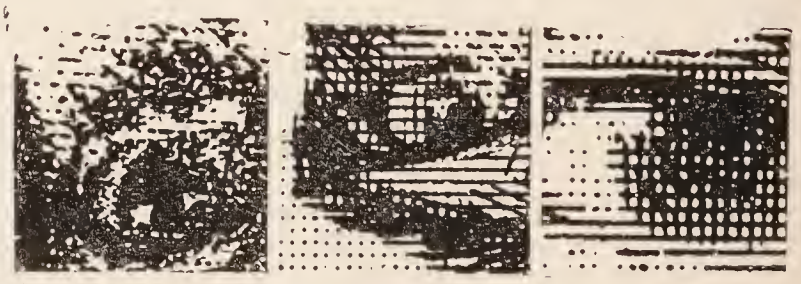
Pen drawings, the copying of which forms a very important part of the work of the photo engraver, are not always strictly 'broken tone.' In certain cases they are so, as for example, in the so-called mechanical drawing, where the lines are of uniform intensity, and also in many other

expressions of the pen of a formal character. Of these it is possible to produce facsimiles, but in work of a more æsthetic character, the definition given does not apply, for the reason that there is shading even in the lines themselves and much of the beauty of the drawings depends upon such variation. The ordinary process of line engraving renders drawings of this character imperfectly, for in the rendering, the forms of the lines only are given, and not the variation in their tone. All the lines in the drawing are reproduced in the printing block, correct in form, in relief, and, in the same plane. When the inking roller passes over the surface all the lines receive ink to the same amount for equal area, and this ink is eventually delivered to paper. The consequence is that lines of different intensity in the original are represented as the same intensity in the copy, with falseness of effect as a result. It is possible by modifying the lines in the etched relief plate by means of the graver to vary the area of metal and thus to vary the amount of ink delivered to the paper, and in this way to alter the intensity of the printed line. For example, a line which prints too dark may be reduced in width, may be split or cut up into dots. In any of these alternatives the effect will be to show a lighter tone in the print. By such means a facsimile of the *effect* of the drawing is possible, so that to the eye the copy *appears* as the original drawing. In order to produce a rendering of the continuous tones or shading of a wash drawing or a nature photograph by means of a type-high printing block, it is necessary to have recourse to a device. This device depends upon the fact that if there be placed upon white paper a regularly disposed series of black dots, the assemblage when examined at such a distance that the angle subtended by the major diameter of the individual dot is exceedingly small, the eye is unable to distinguish between dot and interspaces and, as a consequence, the illusion of a shade of grey will be produced, the depth of the tone depending upon the proportion borne by the area of the black to the area of the white. If the dots are disposed with perfect regularity and are uniform in size, then the tone produced will be uniform over the area, but any variation either in disposition, size, or intensity of the black dots, will result in tone difference. Assume, for the moment, that blackness and disposition are uniform, then variation in size will admit of there being produced a variation in the shading. If a series of tones, say a simply gradated patch of black to white, produced by washing lamp black upon white paper, be imitated in effect to the eye, by applying the foregoing principle, the ' continuous ' tones of the patch are said to have been translated into ' broken ' tone. The effect in the case of the lamp black wash is due to varying absorptions of the incident light by the varying amounts of the pigment ; but in the other instance, the effect is produced by an illusion—by the optical dilution of white with black to produce different shades of grey. The use of this principle is common in graphic representation. It is used by the pen draughtsman ; its effect is seen in steel engravings, in the stipple work of the lithographer and in the shading produced by the juxtaposition of mechanically engraved lines of uniform or varying width and distance apart, which the wood engraver employs, for example, in the pictorial representation of machinery.

Given the dot translation of the graded black and white patch, it may be photographed in the same manner as a line drawing and a type-high block produced in similar fashion.

Prior to the period when the modern method for the rendering of gradation was introduced, broken tone pictures were prepared to give a semblance of shading by a method of drawing upon paper having a paste coating which had been impressed with a grain, regular or irregular, while the surface was in a plastic condition. The draughtsman drew upon this surface with a lithographic crayon, simulating the shading of the original drawing, which was possible by varying the pressure upon his crayon. The absence of planarity in the surface gave isolated patches (irregular dots), instead of smooth tones, which would have been produced had the surface been flat. The finished drawing could now be photographed, transferred to metal by printing by the bichromated albumen process, and afterwards etched type high, or the drawing so made could be treated as a lithographic transfer—the image could be transferred to stone and printed lithographically or to zinc and printed in the same way. Again, if it was transferred to zinc of suitable thickness, it could be etched into relief and printed by letterpress.

Another phase of the same plan consisted in employing chalk-coated paper upon the surface of which was printed a series of fine lines close together, or a fine, regular, or irregular stipple in black in addition to the impressed grain. These were known as ' scraper boards.' The surface of the sheet presented, when examined at the normal distance of vision, a uniform light grey tone. Drawing was effected in the way described, and the coating could be scraped away, so lightening any part. The printed tint saved work in drawing. All parts of the board not touched by the draughtsman remained in semi-tone and this, when contrasted with the high light and shadow, gave the opportunity of suggesting the presence of middle tones by the expenditure of less labour in drawing than would have been necessary had the tint been absent. Scraper board was, at one time, employed for the majority of fashion plates and other drawings for commercial purposes. The illustrations, Figs. *a*, *b*, *c* (Fig. 3), are slightly enlarged representations of portions of drawings produced by this method.



a *b* *c*

FIG. 3.

Modern photo engraving, however, dates from the introduction of a more facile method of translation, which is the optical method of Ives.

This translation is effected in the negative in the manner to be described.

Processes.

Line.—The initial stages in the production of a relief block of a line or other ' broken ' tone drawing are identical with those for the making of a direct photo zincograph (*v. ante, Photo-lithography*) and are directed to the making of a fatty ink image upon the surface of a sheet of zinc. Provided that the metal be sufficiently thick, the image produced for lithography (actually *zinco*graphy) may be etched into relief, or the image produced for relief will serve equally well as the starting-point for lithographic printing.

The processes of line etching now in general use are known by the names of the ' dragon's blood ' process, and the ' roller ' process which was formerly used. Both of these require a print upon the surface of zinc which is prepared by exposing the metal, coated with a very thin film of albumen (or fish glue) and an alkali bichromate, under the negative of the drawing. The exposed print is covered with a thin film of greasy ink, the plate developed in water, and when dry the image is dusted over with finely divided bitumen, which adheres to the ink lines. The excess of the powder is then removed, leaving the metal clean. The plate is now warmed, when the bitumen melts and incorporates thoroughly with the ink. The resist which results is satisfactory for the roller method, but for the ' dragon's blood ' process the ' transfer ' ink used for coating the exposed albumen plates is replaced by a harder and more wax-like ink, and the resist produced is capable of standing a more prolonged etching, which is an advantage in that more relief is produced with which to commence the characteristic operation of the process. The enameline process (see *Tone processes*) is also frequently used for the making of the resist for ' dragon's blood ' etching. In the older roller method, the procedure, after the resist is made, is as follows: The plate is placed for a minute or so in a 1 p.c. solution of nitric acid for the purpose of removing any traces of dirt from the bare parts of the metal, after which it is washed and then wiped over with a sponge charged with a solution of gum arabic. The plate is now rolled up in the lithographic manner with a roller charged with the so-called ' starting ' ink which is usually composed of letterpress ink, beeswax, and lithographic varnish. When the image is strengthened by this ' rolling up,' the plate is dried and is then dusted with a resin—usually ' dragon's blood ' is used—after which the plate is again placed in dilute nitric acid, where it remains until a slight relief is obtained for the covered parts of the metal. The plate is washed, dried, and heated slightly, the effect of which is to cause the wax in the ink to run over the exposed edges of the lines—an operation requiring skill and experience—and the plate is then cooled.

This cycle of operations is repeated usually four times, increasing at each repetition the concentration of the acid, the amount of ink, and the degree of heating of the plate. After the operations described are completed the plate is cleansed. Examination will show that the lines in relief have sloping sides with a step-like formation as shown in Fig 4. The ' steps ' are due to the successive meltings of the ink and subsequent etchings, and are only slightly evident if care and skill are employed by the etcher. These steps must be removed so that the lines may have smooth sloping sides. If the running of the ink has not been properly performed so that the sides are unprotected, they will be eroded or undercut, and as a result the lines will break away in the etching bath or at the least be defective and an imperfect rendering of the drawing will be given. The steps or ' shoulders ' to the lines are removed by the operation of ' finishing ' or ' post ' etching. A hard, glazed leather roller is charged with a strongly resisting ink (composed of good lithographic printing ink, beeswax, and bitumen) and with this a thin film is applied to the surface of the lines of the previously cleaned plate, after which it is placed in dilute nitric acid. This removes the ' step ' near the surface of the line. The plate is washed and dried and again rolled up, but this time the roller is pressed down during rolling so as to coat the straight edge of the side of the line left by the first finishing bath and the plate is again etched until the remaining ' shoulder ' is removed.

In the dragon's blood process, the plate is given a first etch for a longer period than in the

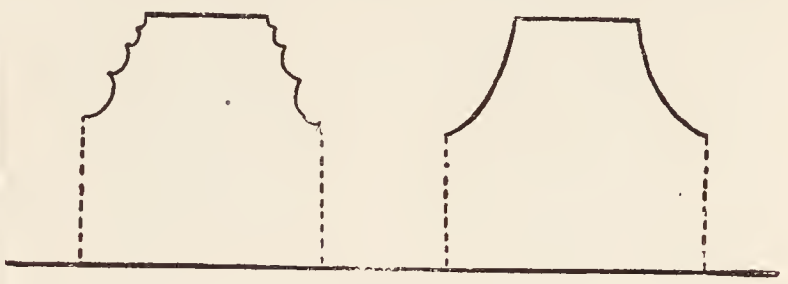


Fig. 4.

roller method. The subsequent protection of the sides of the lines is effected by what is called a ' banking ' of the resin. This banking is made by brushing across the plate, by means of a large flat brush, finely powdered dragon's blood which is, by reason of this operation, mechanically held against that side of the line which faces in the opposite direction to that in which the brush is travelling. The amount of banking is varied by the angle at which the brush is held. When the excess of resin is removed the plate is *gently* heated, when the resin melts sufficiently to stick to the metal, after which it is cooled. The ' banking ' is repeated from the remaining three sides of the plate, so that every line, in no matter what direction it may be, receives protection. The plate must not be heated sufficiently to cause the resin actually to flow. After the sides of the lines are protected, the plate is etched, when the banks of resin gradually break away and the edges of the lines begin to be exposed. The plate is washed, dried, and the protection of the sides again performed, and the etching repeated. These operations are continued until sufficient relief is obtained. To secure adequate protection for the surface of the lines, the plate is usually rolled up once with a resisting ink, the resin afterwards adhering to this, and when the plate is heated incorporating with it.

After the main etching, the plate is cleaned,

and then may require a 'finishing' bath, but the 'finishing' is not required to the same extent as in the plates produced by the roller process.

Etching is generally performed in large earthenware troughs supported upon rockers, by which a see-saw motion is given, but it has become the practice in large establishments to etch by means of etching machines which mechanically deliver a spray or stream of acid against the plate. The etching is more quickly performed, and there are attendant technical advantages.

The advantage of the dragon's blood process lies in its speed and ease, compared with the roller method, and its suitability for machine etching, but it is questionable whether the quality of the printing surface is so good as when the roller process is employed.

Where there are large areas of bare metal, it is necessary to obtain considerable depth, the actual depth being mainly dependent upon the width apart of any two contiguous ink-bearing portions standing in relief. The removal of the metal by etching is lengthy, and is, moreover, wasteful of nitric acid. In modern practice, it is the custom to avoid, as far as possible, this 'deep' etching by removing the metal in the more open spaces by means of a rapidly rotating cutter in the 'routing' machine.

The etched plate is afterwards trimmed, and is then mounted 'type high' upon a block of hard wood or other material, when it is ready for the printer. The satisfactory mounting of the plates is one of the most serious problems of the block maker, there being at present no material which is reasonable in cost which possesses all the necessary qualities of a good mount.

Tone processes ('half-tone' or 'process' blocks).—In these processes we use the principle of translation or continuous tone into broken tone described. Any picture, whether drawing or photograph, may be represented by the half-tone process, which is the most common of modern illustration methods. Given a picture, such constitutes the starting-point, but if an object in relief is to be portrayed, an ordinary photograph must first be made. Except in certain cases—where the range of contrast in the subject is slight—this is the rule. Such photograph is the original. A secondary negative is now made—the original is again photographed—and it is in this second photograph that the translation of tone is made into dot and from this negative the metal printing-surface is produced.

To produce the half-tone negative there is placed, some little distance in front of the sensitive plate, during the exposure in the camera, a sheet of glass having a large number of small apertures, the effect of which is to translate or break up the shading of the ordinary photograph or drawing into dots of various sizes in proportion to the brightness of the tones. This glass plate is termed the 'ruled screen.' It is formed of two plates of flat transparent highly polished glass which are cemented into optical contact. These have, upon their inner surfaces, a series of alternate opaque and clear lines which are usually of equal width, and their direction forms with the sides of each plate an angle of 45°, but from different sides with the two plates. The result is that when the plates are in contact there is produced a series of square transparent openings. The number of lines to the linear inch with different screens varies from 50–250, and as the spaces and lines are equal we have openings equal to $\frac{1}{100}$th to $\frac{1}{500}$th in. The effect produced by the different rulings when the screens are used for negative making is to give a variable number of dots to the superficial inch, each dot corresponding to an opening. The greater the number of dots upon unit area the finer the gradations (detail) in the translation. It may, however, be taken that for few subjects is it necessary to use screens having rulings finer than 175 lines to the inch.

Such screens are made by coating the surface of glass with a resisting medium which is afterwards cut through by means of a diamond point in a special form of ruling machine leaving the glass exposed. Afterwards the plate is subjected to the action of hydrofluoric acid, the resisting medium is cleared away, and the etched lines are then filled in with a black pigment. On completion, there is shown a series of opaque lines upon a transparent ground. Two such plates cemented in contact form the screen, the appearance of which is shown by Fig. 5.

The placing of the screen is not a matter of simplicity, so far as its distance is concerned. The success of the process depends upon the screen being set at the correct distance (d) from the sensitive plate. This distance may be determined as the result of experience, or may be calculated from the expression—

$$d = \frac{bc}{a}$$

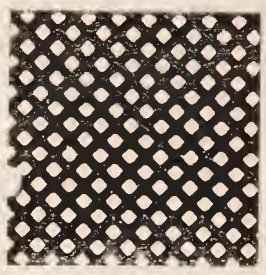


Fig. 5.

where b is the camera extension, c is the width of the screen opening, and a is the diameter of the lens aperture. If the screen be placed in close contact, dots will be produced, but they will be of equal size, and the full gradation of tone will be lost. The dots will also be variable in density with this uniform size while they should be variable in size and uniform in density. If the screen be placed too far away shadow detail cannot be correctly rendered. In the case of excessive distance, the effect of the screen will be wholly lost. In such a position the screen acts, to all intents and purposes, as a sheet of neutral-tinted glass. The success of the process in practice depends, after correct distancing of the screen, upon exposure (which is made in part with one aperture equal in diameter to $\frac{1}{64}$th of the camera extension, and another double that diameter—a plan which is necessary in all cases where there is any considerable range of contrast in the original) and upon the processes of development, reduction or clearing and intensification which follow.

From the negative the print upon metal, which is to form the resist to the etching mordant, is prepared. Usually, for the best class of work, half-tone blocks are prepared upon copper, and the process employed is that known as the 'enameline' or 'fish glue' method. A sheet of polished copper is coated with a viscous solution composed of fish glue (gelatose) and an

alkali bichromate in water, and the resulting film is dried by gentle heat. The coated plate is exposed under the negative, when the portions exposed to light change and become insoluble in water, whilst those parts under the dots remain unaffected and so retain their solubility. After exposure, the plate is washed in cold water until all the soluble portions are removed when the plate is dried. There is now on the surface of the metal a print, the tones of which are produced by dots of various sizes. The metal is strongly heated, when the glue becomes partially carbonised; it is then hard and enamel-like, in which condition, when cool, it is capable of withstanding the mordant—ferric chloride—which rapidly attacks the uncovered metal. Upon etching, the protected parts are left standing in relief, the necessary condition for the printing press. In most cases, the automatic process is assisted by a process of selective or 'fine' etching. If the tones in any part of the plate are not such as will give the desired shades, if for example, the dots are too large, which means too dark a shade in the print, the remaining portions of the etched plate are covered over by a resisting medium applied by means of a brush and the plate is submitted to a further etching. It will be noted that in the description, no mention is made of any protection to the sides of the dots as the etching proceeds, whilst reference to the explanation of the mode of producing line plates will show that elaborate precautions are taken to such end. The actual 'depth' or 'relief' required in a half-tone block is extremely small, for the reason that the ink-bearing elements—the dots—are very close together. But lateral action does take place, with the result that, owing to under-cutting, the size of the dot portion decreases and as a consequence the ink-bearing capacity is lessened and so the dots print lighter. Allowance is made for this in the negative, so that the printed dots on the metal are larger than are required in the finished plate. Upon this lateral action, modification of tone by 'fine etching' depends, for, if the re-etching for any tone be carried far enough, the tone may be brought to almost any degree of lightness of shade. After completing the etching, the plate is cleaned and is mounted type high upon wood.

The continuous tones of a picture may be translated into isolated elements of a less regular order than obtains with the use of the ruled screen, by means of a special form known as the 'metzograph,' due to Wheeler. This is a plate of glass upon the surface of which pyrobetulin has been deposited by sublimation. The coating so produced takes a vermicular form and the surface is afterwards etched with hydrofluoric acid when the glass assumes a similar character, presenting a series of minute cavities, the number per unit area on the 'coarseness' of the screen can be varied. Such a plate appears to the eye faintly translucent. If it be placed in front of the sensitive surface during exposure, the tones are broken up into isolated particles which are distributed with extreme uniformity but without the mechanical regularity of the ruled screen image. The particles vary in size and shape and the absence of the definite and regular dot formation is an advantage in the reproduction of many classes of originals. The negatives are employed in the same way as those made by the ruled screen. The character of the 'texture' produced by the two methods is shown in Fig. 6, *a* and *b*, by which comparison may be made.

Other forms of irregular grain screens are employed which have opaque grains and perform their function by a similar principle and the ruled screen. The 'metzograph' screen forms a negative by reason of the peculiar surface which refracts the light so as to form a grain.

Three-colour printing by relief blocks.—The principles upon which colour is rendered by the so-called 'three-colour' process are given under the heading of colour photography (*v. ante*), and it is only necessary here to show how these principles are utilised in the making of prints by letterpress. Briefly, the method consists in making three negatives through colour screens, one for each colour sensation, and from the negatives, blocks are prepared which are printed on the principle of superimposition in inks approximately complementary to the sensation hues.

Two processes are employed, the indirect and the direct. In the former, ordinary continuous tone three-colour negatives are made, and from these transparencies by contact from which the three half-tone dot negatives are produced. Or, in the direct process, the dot negatives are made direct from the object upon



a *b*

Fig. 6.

special dry plates which are panchromatic (*see* The Dry Plate as a Recording Surface, p. 221) and also suitable for ruled screen negative making. Such negatives may also be made upon colour sensitised collodion emulsion. There is a slight complication in making the negatives owing to the fact that if there be printed two or more impressions one above the other from half-tone blocks (or indeed from any printing surface where the colour is distributed in the form of elements in perfectly regular order), a pattern is produced—the so-called *moirê* effect—which is very objectionable. This pattern cannot be avoided, but it may be reduced to an almost negligible form if it be arranged that the lines of dots (forming the half-tone picture) in the separate printings cross at a particular angle which is secured by the positions of the ruled screen when the negatives are made. The direct process is only applicable to the photography of flat objects. If the object is in relief the indirect process must be employed. In any case, the negatives forming the set must have images equal in size. Blocks are prepared upon copper by the enamelline process. Successful three-colour work is very largely a matter of skilful fine etching, but the amount required is frequently in excess of that which would be required were more care bestowed upon the

making of the negatives. The plates, when finished, are accurately trimmed and mounted, and are afterwards printed in ink of the hues yellow, crimson, and greenish-blue. At the present time, the sensitive plates obtainable well fulfil the theoretical requirements, but the same cannot be said of the printing inks.

On the Continent more than in Great Britain and the United States, at the present time, four-colour processes are employed with considerable success. A set of blocks may be prepared by the three-colour method and a fourth block made from the original, from a negative made through the ordinary 'yellow' screen, which is employed for the additional printing, the colour being generally a grey of a tone to suit the subject. The extra printing from a block prepared by skilful hands is a valuable aid and serves to soften the crudity of colour which is so frequently a fault in pictures produced by the orthodox three-colour process.

Preparation of drawings and photographs.—The translation of any picture by screen methods always leads to a flattening of the contrast. Although 'fine etching' of half-tone plates is to a considerable extent employed to alter the appearance of the pictures as presented by the proofs from the plates—of illustrations, indeed, which are not satisfactory to those who wish to use them even before they are reproduced—the process would, to some extent, be necessary in the case of good originals because of the flattening effect of the screen. When drawings are to be reproduced by these methods and have to be made for the purpose, allowance is generally made for the reduced contrast by forcing the effect in the drawing, hence 'drawings,' for process, which are generally made in monochrome body colour although useful for the purpose intended, are of little value afterwards for obvious æsthetic reasons.

Any drawing in line, even those made without any regard to reproduction processes, where beautiful effect is the only consideration, may be successfully translated, but only by the expenditure of extra time and skill. Disregarding pictorial drawings, much technically unsatisfactory 'copy' is dealt with in the ordinary way. When drawings in line are made, however, with a view to reproduction in the commercial way, they are generally prepared in black line upon white card.

By far the larger amount of half-tone illustrations to catalogues (especially those showing machinery) and publications of a similar commercial character are prepared from photographs which have been 'worked up' by the draughtsman, who changes the appearance of the original by modifying portions, by suppression, or by addition, and this to such an extent that the photograph is completely changed. Such 'working up' is carried out by means of the 'air brush,' a pen-like tool by means of which a fine stream of air can be caused to project a spray of liquid pigment upon a surface, the effect producible being entirely under control, and moreover—which is the important feature—with that smoothness and continuity which is a characteristic of the shading in a photograph, so that the added work is in harmony with the print. It is largely owing to this that the photo-engraver has almost entirely replaced the wood engraver in the preparation of the illustrations for the best classes of catalogue.

The author desires to acknowledge the considerable assistance he has received from his colleague, Mr. R. B. Fishenden, in the preparation of this section upon Photo-Mechanical Processes.

C. W. G.

PHOTOLITHOGRAPHY *v.* PHOTOGRAPHY.

PHOTOPHONE *v.* SELENIUM.

PHOTOSANTONIC ACID *v.* SATONICA.

PHOTOSYNTHESIS AND PHYTOSYNTHESIS. *Historical.*—The first observations of note in connection with phytosynthesis were made by de la Haire in 1690, and Bonnet in 1754, who found that green plants or leaves immersed in water and exposed to sunlight gave off bubbles of gas. In 1771 Priestley (Phil. Trans. 1772, 62, 168, 193) commenced his investigations of the influence of plants on the composition of the air around them. It was in August, 1771, that he carried out in Leeds his memorable experiment of placing sprigs of mint in air which had been vitiated by the burning of a candle or by animal respiration. This observation led him to conclude that plants, instead of affecting air in the same way as animals do by respiration, reverse these effects and tend to render the atmosphere sweet and wholesome after it had become noxious as the result of animals living or dying and putrefying it. In 1779 Priestley published the results of his later work, which, however, were not altogether confirmatory of those arrived at six years before. This want of consistency was due to his failure at that time to recognise the important influence of light, an explanation that was given shortly afterwards by Ingen-Housz.

In his experiments with plants immersed in water, Priestley observed the fact, already noted by de la Haire and by Bonnet, that bubbles of gas arose spontaneously from the leaves and stems, and it occurred to him that an examination of the nature of this gas by his new eudiometric process ought to settle the question whether plants really do contribute in any way to the purification of ordinary air. It was in June, 1778, that he put this to the test, when he found that the air thus liberated was much richer in oxygen than ordinary air. On removing the plants he found to his astonishment that the water in which they had been placed, and which had a considerable amount of green matter adhering to the sides of the phials, still continued to evolve a gas which increased in amount when the vessels were placed in sunlight. On testing this gas he found that it consisted to a great extent of oxygen. From other observations he was led to make a series of experiments with water artificially impregnated with carbon dioxide, and these left no doubt in his mind that the production of the green matter and the evolution of oxygen were in some way due to the presence of carbon dioxide. Up to this point Priestley was following a path which seemed about to lead him to a complete solution of his previous difficulties. He had succeeded beyond all question in showing, not only that the evolution was dependent on the pre-existence of carbon dioxide, but that light was also required for the process. It only required the recognition of the vegetable nature of the algæ which constituted

his green substance to bring these observations into line with his previous work, and to complete the discovery which would have eclipsed in importance all those others with which the name of Priestley is associated. It was just this one step which he most provokingly failed to take. Meanwhile the subject had been taken up by two other observers, Ingen-Housz and Senebier.

Ingen-Housz, in 1779, published a treatise entitled Experiments upon vegetables, discovering their great power of purifying the common air in the sunshine and of injuring it in the shade and at night. In this he demonstrated that the amelioration of the surrounding air by plants is not as Priestley at first believed due to vegetable action *per se*, but is dependent on the access of light of a sufficient degree of intensity, and, moreover, that the power is confined to the green part of the plant. He was the first to show that the green parts of the plant in the dark, and the roots both in light and darkness, vitiate the air in the same way as do animals. He understood that in this vitiation carbon dioxide played a part, but he was not sure if the evolution of carbon dioxide was a continuous process as in the case of animals.

Senebier (1782–1800) proved beyond all doubt that the evolution of oxygen depended upon the pre-existence of carbon dioxide, and that the more the water was saturated with carbon dioxide the more oxygen was evolved from the algæ employed in his experiments.

In about 1796 Theodore de Saussure commenced his researches and published his results in a small volume entitled Recherches Chimiques sur la Vegetation, which must rank as one of the great classics of scientific literature. De Saussure was a past-master in the art of experiment, and, indeed, the methods which he devised for demonstrating the influence of water, air, and soil on vegetation have been the models on which all later investigations have been based. He not only proved that gaseous carbon dioxide is decomposed and the carbon assimilated, but also that the volume of oxygen disengaged is approximately equal to that of the carbon dioxide decomposed. That atmospheric carbon dioxide is not only beneficial to plants in sunlight, but is also essential to their very existence de Saussure proved by introducing an absorbent into the vessel containing a plant or the branch of the tree rooted naturally in the soil. He was therefore the first accurately to demonstrate the fixation of carbon dioxide, and to recognise that the oxygen evolved is due to decomposition of this gas. It is a remarkable fact that the rigid experimental proof which de Saussure brought forward in support of his views did not carry conviction to the minds of every one. Thus when von Liebig took up the question in 1840 he found that the doctrine of carbon assimilation as taught by de Saussure had given place to the humus theory of Treviranus, a theory which no longer took any account of the decomposition of carbon dioxide by the leaves, but which derived the whole of the elements of the growing plant from a solution of the soil extract absorbed by the roots. Von Liebig once more established the doctrine of carbon assimilation as enunciated by de Saussure, as also did Dumas in France, and finally Boussingault gave the death-blow to the humus theory by his confirmation of de Saussure's experiments on the equivalence of the oxygen evolved and the carbon dioxide absorbed. Boussingault was also the first to express the opinion that sugar is the direct result of the assimilation process. By his careful experimental work von Mohl drew attention to the formation of starch grains in the chlorophyll-corpuscles which he said was of almost universal occurrence, and Sachs, in 1862, expressed the opinion that the appearance of starch in the chloroplasts is a function of assimilation, and he proved this by showing that the formation of starch grains is dependent upon exposure to light. Godlewski next showed that the formation of starch in the chloroplast cannot under any circumstances take place in an atmosphere free from carbon dioxide. Further, he demonstrated that in a carbon-dioxide-free atmosphere, even under strong illumination, the starch in the chloroplast slowly disappears just as it does in plants growing in ordinary air in the dark. Sachs was therefore justified in concluding that the formation of starch in the assimilating organ is a consequence of the decomposition of the carbon dioxide during assimilation, and that in this way the increase of weight which takes place in plants during assimilation can be satisfactorily explained. In 1883 Böhm made the interesting discovery that when green leaves are placed in the dark until the starch of their chloroplastids has completely disappeared, there is a reappearance of starch when the cut end of the leaf stalk is immersed in a solution of cane sugar and of glucose, or when the leaf is brought directly in contact with solutions of these substances. In fact, although under ordinary conditions the materials for plant-growth are manufactured by production of carbon dioxide, under other conditions the cell can supply its requirements from suitable ready-made organic substances. These observations were fully confirmed two years later by Schimper, and were subsequently much extended by A. Meyer and E. Laurent, who found that fructose, maltose, mannitol, dulcitol, and glycerol can also contribute directly to the nutrition of leaves. Bokorny further found that starch production in the chlorophyll body can be induced by a large number of organic substances, but by far the most important of his results is the proof that formaldehyde is also directly assimilable.

There is no doubt that this experimental work establishes the manner in which assimilation occurs in the plant. Under natural conditions it consists of the absorption of carbon dioxide by the chloroplastids and its reduction by the chlorophyll in the presence of water and sunlight to form sugars. The first stage in the development of the subject has thus been reached, and the second stage consists in the study of the chemistry of the process which naturally includes the function of the chlorophyll. It is obvious that in order to obtain any satisfactory explanation of the rôle played by the chlorophyll the constitution and, above all, the reactions of the substance must be known. Although many theories were advanced by the earlier investigators, these were based on incomplete knowledge and consequently they were for the most part highly speculative and need not be discussed. The first advance was made by von Baeyer in 1870 (Ber. 3, 68), who put forward

his famous hypothesis that the first produet of assimilation is formaldehyde, produced by the photolysis of earbon dioxide in the presence of water with evolution of free oxygen. He suggested that the ehlorophyll decomposes the carbon dioxide to earbon monoxide and oxygen, and that the latter eombines with the chlorophyll, whilst the former is redueed to formaldehyde which then undergoes polymerisation to earbohydrates. Plausible as this hypothesis is of formaldehyde being the first substanee produeed, it is only reeently that its correetness has been proved. Many investigations have been earried out with the view of testing this hypothesis, and these have been of two kinds. On the one hand innumerable attempts have been made to prove the presenee of formaldehyde in the green leaf, and, on the other hand, many experiments have been earried out on the reduetion of carbon dioxide *in vitro* and the formation of formaldehyde. In spite of the great number of statements that are met with in the literature to the effect that free formaldehyde exists in the leaf the problem remained very mueh as it was. In every ease where the presenee of free formaldehyde appeared to be established it could readily be explained as being derived from sources other than assimilation. Mention may be made of Schryver's work, whieh led him to state that formaldehyde is to be found within the ehlorophyll, but not distributed through the whole leaf. This, however, was disproved by Willstätter, who repeated the experiments with *pure* ehlorophyll. A eontribution whieh aroused much interest was that published by Usher and J. H. Priestley in 1906 (Proe. Roy. Soe. 77 B, 369; 78 B, 318; 1911, 84 B, 101). Aecording to their results formaldehyde and hydrogen peroxide were eonsidered to be the normal photolytie products, the former being rapidly polymerised and the latter deeomposed by a speeial enzyme with the liberation of oxygen. The important statement in their work was that the initial step of deeomposing the carbonie aeid in the chloroplastid is independent of vital or enzymic activity. Their experiments were carried out with green leaves of Elodea, in whieh both protoplasm and enzymes had been killed by immersion in boiling water. In the presenee of light these were said to be eapable of produeing formaldehyde from earbonic aeid. In other words, the effieiency of the ehlorophyll-apparatus aceording to this view is not destroyed by eliminating the vital ageneies, but owing to the non-removal of the photolytic produet the aeeumulated hydrogen peroxide kills the chlorophyll and the reaction then becomes reversible. These views were sharply disputed by Ewart (Proe. Roy. Soc. 1908, 80 B, 30), Warner (*ibid.* 1914, 87 B, 378), and Wager (*ibid.* 1914, 87 B, 386), and finally, Willstätter was able to show that the production of the formaldehyde in these experiments was due not to the chlorophyll but to many other substanees contained in the chlorophyll.

The reduction of carbon dioxide without the agency of chlorophyll has formed the basis of many investigations. Although this has actually been earried out by a great variety of methods, these have no direet bearing on the eonditions existing in the plant. In 1893 Bach (Compt. rend. 1893, 116, 1145, 1389) obtained formaldehyde and uranium peroxide by the action of earbon dioxide on uranium acetate in sunlight. Löb (1905–1906) (Zeitseh. Elektroehem. 11, 745, 12, 282) was able to show that under the influenee of the silent electrie diseharge carbon dioxide or earbon monoxide together with hydrogen and water yield formaldehyde and a condensation produet whieh he believed to be glyeollie aldehyde. D. Berthelot and Gaudechon in 1910 (Compt. rend. 150, 1690) obtained formaldehyde by the action of ultra-violet light on a mixture of earbon monoxide and hydrogen. In 1906 Usher and Priestley repeated Bach's work and confirmed it. In 1911 Moore and Webster (Proc. Roy. Soe. 1913, 87 B, 163, 556; 1919, 90 B, 168) again took up the question and showed that formaldehyde is produeed when solutions of carbonic aeid, eontaining collodial uranium hydroxide or ferric hydroxide, are exposed to light. Sinee they found the same results when eertain inorganie salts replaced the eolloidal hydroxide, they eoneluded that, in order to synthesise formaldehyde from earbonic acid, an inorganic catalyst is necessary, the function of which is to convert the light energy into the chemieal energy neeessary for the highly endothermic reaction $H_2CO_3 = CH_2O + O_2$. Impressed by their results with colloidal ferric hydroxide these authors were convineed that iron plays an important rôle in the assimilation process. Since it has also been found that iron is actually necessary for the synthesis of ehlorophyll, seeing that the leaves of plants starved of iron suffer from ehlorosis, Moore and Webster stated that iron salts are more fundamental to photosynthesis and take an earlier share in it than ehlorophyll. These views are very different from those whieh have resulted from the earlier work. In the first place, the theory of von Baeyer that the moleeule of carbon dioxide is photolysed into earbon monoxide and oxygen, the earbon monoxide being subsequently reduced to formaldehyde, is supplanted by the theory of the photosynthetic conversion in one stage of earbonie acid into formaldehyde and oxygen. In the second place, the function of the chlorophyll is made seeondary to the eatalytie effect of iron salts. Whilst it is proved by the most reeent work that the photosynthetie reaetion eonsists in the eonversion of the earbonic aeid into formaldehyde, Moore and Webster's theory of the funetion of iron-salts has been found to be ineorreet, the real catalyst being ehlorophyll.

In 1913 Willstätter (Willstätter and Stoll, Untersuchungen über Chlorophyll, Berlin, 1913) published a eomplete aeeount of his investigations into the constitution of chlorophyll whieh established the fact that the naturally oeeurring substance is a mixture of two pigments, the blue-green chlorophyll A and the yellow-green chlorophyll B, which can be separated from one another. These two pigments are complex magnesium-compounds of similar constitution—

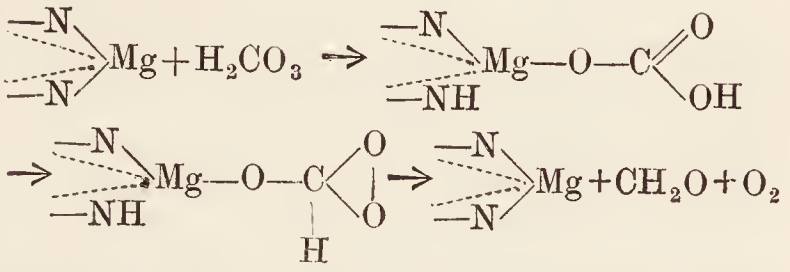
Chlorophyil A. $(MgN_4C_{32}H_{30}O)CO_2CH_3 \cdot CO_2C_{20}H_{39}$
Chlorophyll B. $(MgN_4C_{32}H_{28}O_2)CO_2CH_3 \cdot CO_2C_{20}H_{39}$.

Willstätter (Willstätter and Stoll, Untersuehunger über die Assimilation der Kohlensaüre, Berlin, 1918) next carried out an exhaustive study of the assimilation of earbon dioxide by the green leaf, and he re-investigated in detail all earlier work and discussed the validity of the

theories that had previously been enunciated. He showed that two pigments, the hydrocarbon carotin $C_{40}H_{56}$, and xanthophyll $C_{40}H_{56}O_2$, always accompany the chlorophyll in green plants. Although the chlorophyll content of normal green plants varies somewhat, the ratio of the chlorophyll components to one another is remarkably constant, even during assimilation. The carotinoids also show no marked variation in the relative amounts of the two present in different plants. Willstätter discusses the function of these in the photo-assimilation process, and concludes that if they take part at all it is in an indirect way, since he found that the assimilation proceeds equally well if the light they absorb is excluded. This conclusion, however, was based on insecure evidence, since it is very doubtful whether the screen he used was effective in completely excluding the light rays which are absorbed by carotin and xanthophyll.

Two very important statements are made by Willstätter as the result of his work. During intensive and protracted illumination the ratio of chlorophyll A to chlorophyll B remains constant, whilst the ratio of xanthophyll to carotin increases, that is to say, some carotin is converted into xanthophyll. Further, apart from the constancy of the ratio of chlorophyll A to chlorophyll B, the total quantity of mixed chlorophyll never decreases during assimilation. This last observation disposes of the hypothesis advanced by Ewart and by Wager, that photosynthesis is due to the decomposition and reformation of the chlorophyll. As regards the rate of assimilation Willstätter shows that this varies enormously in young, fully grown, and old leaves, and also that a similar variation as regards the influence of temperature and illumination takes place in leaves rich and poor in pigment. With leaves rich in chlorophyll increase of light intensity does not affect the assimilation, whereas increase in temperature increases the assimilation. On the other hand, with leaves poor in pigment the effect of temperature is negligible, whilst increase of light intensity greatly increases the rate of assimilation. From these experiments Willstätter concluded that a second chemical substance must be present in the chloroplast before assimilation can take place, this substance probably being an oxidising enzyme, or a peroxidase. Willstätter also investigated the reactions of chlorophyll towards carbon dioxide both in the leaf and *in vitro*. Whereas chlorophyll is not acted upon by dry carbon dioxide it combines with carbonic acid to form an addition compound that is readily dissociated. Chlorophyll in solution in organic solvents shows no reactivity towards carbon dioxide, but in colloidal aqueous solution a reaction occurs in which the magnesium is precipitated as carbonate, but there is first formed the labile addition compound of chlorophyll and carbonic acid which can dissociate and regenerate chlorophyll. Since the colloidal condition is analogous to the condition present in the chloroplast, it must be concluded that the easily dissociated addition compound has a definite function in the assimilation process. A leaf can absorb up to 20–25 volumes p.c., but this quantity of carbon dioxide decomposes the chlorophyll in aqueous colloidal solution. The chlorophyll carbonic acid complex in the leaf therefore must be protected in some way against dissociation as also against hydrolytic decomposition.

In formulating a theory of the rôle played by the chlorophyll in the assimilation process, Willstätter first of all proves conclusively that the molecular ratio of carbon dioxide absorbed to oxygen evolved is exactly 1 : 1, and he points out that this definitely proves that the first product is formaldehyde, since the formation of any other product would require a ratio greater than 1 : 1. Such alternative suggestions were made by von Liebig (Annalen, 1843, 46, 66) and by Baur (Zeitsch. physikal. Chem. 1908, 63, 683), who favoured the formation of oxalic acid, whilst Brunner and Chuard (Ber. 1886, 19, 595) thought that glyoxylic acid was the first product. Willstätter's theory is that whilst the colloidal condition of the chlorophyll and its optical properties are not affected by the combination with carbonic acid, the addition compound is transferred by the absorption of light energy into the isomeric formaldehyde peroxide compound.



This is then acted on by the enzyme which regenerates the chlorophyll and sets free formaldehyde and oxygen.

Photosynthesis of formaldehyde and carbohydrates from carbonic acid.—In reviewing the historical development of the study of phytosynthesis it becomes obvious that no real explanation has been offered of any of the theories that have been from time to time put forward. Even Willstätter, in spite of his brilliant experimental work, has carried us very little further than von Baeyer stood in 1870. He certainly has proved beyond question that the first step in phytosynthesis is the absorption of atmospheric carbon dioxide and its conversion by light into formaldehyde, but how this change occurs he fails to prove. There still remain the old obstacles of the total absence of free formaldehyde in the leaf and the failure to reproduce the reaction in the laboratory under conditions similar to those in the plant. It is very striking how the improvement in experimental technique tends more and more definitely to prove both that formaldehyde is produced and that it does not exist in the leaf. Even were there to hand a complete explanation of these abnormalities there still remains unbridged the gap between formaldehyde and the carbohydrates. Beyond this still there lies the synthesis of the nitrogen compounds—protoplasm, protein, and alkaloid—whose origin seems more mysterious still. Small wonder is it that the theory of the *vis vitalis* held its sway so long on man's imagination, for it is borne in on all that the chemistry of the living organism seems almost to be a thing apart from the chemistry of substances inanimate. Yet after all the secret was not far to seek and is only one of energy. It were idle to deny the great advance in chemistry if such be measured

by the number of new compounds added to the list, but if it be measured by the growth of understanding of chemical reaction the advance has been but small. Until recently much has been hidden in chemistry because of the want of knowledge of the energy changes which play so great a part in all reaction. Indeed, it is not too much to say that Planck's great theory of energy quanta and its application to chemistry mark as great an epoch in the history of the science as that when John Dalton first conceived his material quanta and founded the atomic theory.

There is no need to enter into a discussion of this theory, but one of the most important deductions from it must be mentioned, a deduction which has found very strong experimental support. In general, a molecule in the free state exists in a phase that is non-reactive, and in order to carry out any reaction it is first of all necessary to bring the molecule into a reactive phase. This, which is the first stage of the reaction, requires that a definite amount of energy be supplied to each molecule, the amount necessary being the difference in the energy contents of the initial phase and the particular phase required for the reaction in question. Each consecutive phase of a given molecule differs in energy content by a fixed quantity of energy characteristic of that molecule, and this is called the molecular quantum of energy. It follows that the amount of energy necessary to activate a molecule must always be exactly one or more of its molecular quanta. The first stage of the reaction therefore can be represented by the equation

$$A+E=A'$$

where A is the molecule in its non-reactive phase, A′ is the activated molecule, and E is the energy which must be absorbed in order to effect the change of phase. The second stage of the reaction is the atomic re-arrangement, whereby new molecules are produced. During this stage energy is evolved, and it may be represented by the equation

$$A'=B'+F$$

where B′ is the freshly synthesised molecule, and F is the energy evolved. Now the molecule B′, being freshly synthesised, exists in a phase of high energy content and is therefore metastable. The third and final stage then ensues, in which the molecule B′ loses energy and passes into its normal and non-reactive phase B

$$B'=B+G$$

Just as in the first stage where E is exactly equal to one or more molecular quanta characteristic of the molecule A, so also in the second and third stages F and G are exactly equal to one or more molecular quanta characteristic of the molecule B. The sum of these three stages is, of course, the ordinarily accepted equation of the reaction

$$A=B+K$$

where the energy $K=F+G-E$. If the sum of the two amounts of energy evolved in the second and third stages is greater than that absorbed in the third stage the reaction is exothermic, whilst an endothermic reaction is one in which the energy necessary for the first stage is greater than the total amount evolved in the second and third stages.

This deduction from the energy quantum theory and the recognition of the three stages of any reaction is of supreme importance, since it correlates all reactions and shows that in order to induce any reaction it is first of all necessary to supply energy to the system so as to activate the molecules, this being true however exothermic the reaction may be. There are three methods by which the energy necessary for the first stage may be supplied. It may be supplied by a material catalyst, or as radiant energy either in the form of heat or light. The action of a catalyst does not arise here, and need only be mentioned in order to guard against any misconception. Many reactions take place in solution without the apparent intervention of the first stage, but in such cases the molecules have been activated by the solvent which functions as a catalyst. In general it is a matter of little consequence whether a molecule is activated by heat or light, that is by infra-red or ultra-violet rays, in view of the known integral relationships that exist between the frequencies at which a molecule can absorb energy. It is a matter of cardinal importance, however, in the case of highly endothermic reactions, in which the increment of energy necessary for the initial phase change must obviously be a large number of molecular quanta. When a molecule absorbs energy at its principal frequency in the infra-red it absorbs it in terms of its molecular quantum, but if it absorbs ultra-violet light the unit of energy absorbed is a quantum which is an integral multiple of the molecular quantum, the multiple depending on the phase in which the molecule exists. One single quantum of energy absorbed at the characteristic frequency in the ultra-violet is always sufficient to activate a single molecule for any reaction however endothermic this may be. An endothermic reaction, in the first stage of which each molecule requires a large number of molecular quanta to activate it, will obviously be very much easier to carry out by exposing the molecules to energy of their characteristic frequency in the ultra-violet, when the absorption of one quantum per molecule is sufficient, than by exposing them to infra-red radiation when the reaction will not proceed until a specific number of quanta have been absorbed by each molecule. When, as is frequently the case, this specific number is 10 or more, it is not surprising that the realisation of the reaction by means of heat becomes impossible from the practical standpoint. Such a reaction, however, is readily brought about by the absorption of a single quantum by each molecule at its characteristic frequency in the ultra-violet. This may be understood more clearly from a specific instance of an endothermic reaction, namely, the decomposition of hydrogen chloride into hydrogen and chlorine. The molecular quantum of HCl is about $5{\cdot}7\times10^{-13}$ erg, whilst the quantum absorbed at the ultra-violet frequency is about $9{\cdot}7\times10^{-12}$ erg, which is 17 times as large. The activation of a HCl molecule so that it may decompose requires 17 molecular quanta, and this may readily be brought about by exposing the gas to radiant energy of the wave-length $203\mu\mu$, when the absorption of a single quantum per molecule is sufficient. In order to bring about this reaction by heat it will be necessary

for each molecule consecutively to absorb 17 molecular quanta, without losing any by radiation during the process, before it can decompose. The preparation of hydrogen and chlorine from hydrogen chloride is therefore very difficult to carry out by the aid of heat, but is readily induced by light of very short wave-length.

As was stated in the historical introduction there are very strong arguments in favour of the fact that the first step in the phytosynthetic process in the living plant is the production of formaldehyde from carbon dioxide and water. The synthesis of formaldehyde from carbonic acid is, however, a hightly endothermic reaction, since the heat of combustion of formaldehyde, which is the reverse reaction, is of the order of 145,000 calories. The minimum increment of energy therefore required to activate the molecule of carbonic acid so that it may give formaldehyde and oxygen, when expressed in calories per gram molecule, must be about 150,000 calories. It is obvious therefore that this reaction cannot be realised by the everyday methods of the laboratory, since the energy E required to activate a molecule of carbonic acid is 25 of its molecular quanta. On the other hand, carbonic acid is able to absorb light of very short wave-length ($\lambda=200\mu\mu$), and a single energy quantum per molecule at this frequency corresponds almost exactly with 150,000 calories per gram molecule. Although this reaction cannot be induced by the ordinary laboratory methods, it should be realisable by means of light of very short wave-length, and this has been shown to be the case in experiments carried out in Liverpool (Baly, Heilbron and Barker, Chem Soc. Trans. 1921, 119, 1025; Baly, J. Soc. Dyers and Colourists, 1921, 38, 4; Nature, 1922, 109, 344; Heilbron, J. Soc. Chim. Ind. 1922, 41, 89 R). If carbon dioxide is passed through water which is exposed to ultra-violet light of wave-length $\lambda=200\mu\mu$ formaldehyde is produced, and therefore one of the great difficulties in connection with the acceptance of von Baeyer's theory is removed.

Although the synthesis of formaldehyde has been photochemically carried out in the laboratory with light of wave-length $200\mu\mu$, this is certainly not the case in the plant, for there is present in sunlight no radiation of this wave length. The plant must in some way carry out the reaction with the absorption of visible light, because it is well known that visible light only is necessary for the photo-assimilation of carbon dioxide. Now it has been further found experimentally that if a visibly coloured basic substance is added to the aqueous solution of carbon dioxide formaldehyde is produced on exposing the mixture to visible light. The coloured substance being basic forms a complex with the carbonic acid, and within such a complex the components possess an identical infra-red frequency, that is to say, the molecular quanta of the two are identical. The energy absorbed by the coloured component is radiated at this common infra-red frequency and re-absorbed by the carbonate component. The necessary increment of energy is thus gained by the carbonate component which is converted into a molecule of formaldehyde and a molecule of oxygen. This type of reaction has been named photocatalysis, the coloured substance acting as photocatalyst. It has been proved that malachite green and *p*-nitrosodimethyl-aniline act as photocatalysts in this reaction, and in the presence of carbon dioxide give formaldehyde on exposure to visible light.

It has been shown by Willstätter that chlorophyll as it occurs in the plant combines with carbonic acid, and hence there is no doubt that it functions as a photocatalyst. The green-coloured complex absorbs visible light, and the energy so absorbed is transferred to the carbonic acid through the identity of infra-red frequency, with the result that formaldehyde and oxygen are produced. Although this gives a satisfactory explanation of the mechanism, by means of which the living plant is able to produce formaldehyde with the aid of visible light alone, the story is far from complete, for there are yet to be considered the details of the process, whereby the oxygen set free in the photosynthetic operation is transpired as gaseous oxygen, a process which is of great importance in view of the energy changes involved. Willstätter has shown that chlorophyll is a mixture of two substances, chlorophyll A and chlorophyll B, and that a molecule of chlorophyll B contains one atom of oxygen more and two atoms of hydrogen less than a molecule of chlorophyll A. Two atoms of oxygen therefore are required to convert a molecule of chlorophyll A into a molecule of chlorophyll B, and since this is the exact relation required in the photosynthetic operation it is impossible to believe that this is not a fundamental part of the process. It is in the highest degree probable that a molecule of chlorophyll A combines with a molecule of carbonic acid, and that this complex on exposure to the light gives a molecule of activated formaldehyde and a molecule of chlorophyll B. Willstätter did not accept this view, because he found that the ratio of chlorophyll B to A is not altered during photosynthesis, but since he also proved that the velocity of transpiration of the oxygen is exactly equal to that of the absorption of carbon dioxide, this cannot be accepted as evidence. It only means that there is present in the leaf some mechanism whereby the chlorophyll B is de-oxidised and re-converted into chlorophyll A. Willstätter has further proved that an aqueous solution of chlorophyll saturated with carbon dioxide decomposes on exposure to light, no measurable photo-assimilation of carbon dioxide taking place. This affords an additional proof that there is present in the living plant a mechanism for maintaining the chlorophyll equilibrium. In the living photosynthetic cell there exist along with the chlorophyll the two pigments, carotin $C_{40}H_{56}$ and xanthophyll $C_{40}H_{56}O_2$, the relation between the two as regards oxygen being the same as that between chlorophyll A and B. It may therefore be suggested that carotin has the power of reducing chlorophyll B to chlorophyll A, itself being oxidised to xanthophyll. This is supported by Willstätter's observation that the ratio of xanthophyll to carotin is increased during the photosynthetic operation. This increase though perfectly definite is not large enough to decrease materially the amount of oxygen transpired.

As was pointed out above, the complete reaction $H_2O+C_2O=CH_2O+O_2$ is highly endothermic and is accompanied by the absorption

of about 145,000 calories per gram molecule of formaldehyde produced, and it is interesting to note that one quantum of energy absorbed in the visible region by chlorophyll cannot be sufficient to induce the complete reaction, since in the absence of the chlorophyll as photocatalyst the reaction requires one quantum per molecule at $\lambda=200\mu\mu$, which corresponds to 150,000 calories per gram molecule. There are two possible explanations of this discrepancy. On the one hand certain quantitative investigations have shown that the carbonic acid may be partially activated by its combination with the chlorophyll. Alternatively it is more probable that, whilst one quantum of energy at $\lambda=200\mu\mu$ is required for the complete reaction with the escape of free oxygen, one quantum of visible light as absorbed by the chlorophyll is sufficient to induce the reaction

$$\text{Chlorophyll A}+H_2CO_3=\text{Chlorophyll B}+CH_2O$$

It is hardly necessary to point out that either of these alternatives amplifies the principle of photocatalysis as previously defined. In either case the completion of the reaction, whereby oxygen is abstracted from the chlorophyll B and transpired into the atmosphere, must require a further supply of energy. This second amount of energy is doubtless absorbed as light by the carotin and xanthophyll, the absorption bands of which lie in the visible region and between those of chlorophyll, so that each can simultaneously and independently absorb visible light. This suggested explanation is now being investigated in Liverpool.

Mention was previously made of the insecurity of the evidence on which Willstätter based his statement that photo-assimilation proceeds when the leaf is screened from the rays absorbed by carotin and xanthophyll. The screen he used was an aqueous solution of potassium bichromate, but a quantitative measurement of the absorptive power of this substance shows that it by no means absorbs all the rays that affect the two natural pigments. Further, Moore and Webster's statement that a catalyst is necessary for the production of formaldehyde from carbonic acid has definitely been proved to be incorrect, since the reaction takes place whether the catalyst is present or not and is not increased in velocity by the catalyst. Colloidal ferric hydroxide, however, may act to a small extent as a photocatalyst, owing to the formation of a carbonate, but the conclusion drawn by these authors that iron salts play a more important rôle in the plant than chlorophyll is quite unsound, as Willstätter has clearly proved. The effect of chlorosis caused in the leaves when the plant is starved of iron salts is most probably to be explained by the fact that they aid the synthesis of pyrrole which enters so largely into the constitution of chlorophyll. This is exactly analogous to the therapeutic value of iron in cases of anæmia in man, hæmoglobin and chlorophyll having been shown by Willstätter to be similar in their constitution.

It must not be forgotten that, although the above offers an explanation of the photosynthesis of formaldehyde in the living plant which rests on a secure quantitative basis of energy relationships (Baly and Barker, Chem. Soc. Trans. 1921, 119, 653), there still remains the fact that free formaldehyde does not exist in the growing leaf and, indeed, is an active poison to plants. It must, however, be remembered that these statements refer to formaldehyde in its normal form, and that when first produced by photosynthesis it exists in a phase of high energy content. In short, as far as its actual synthesis is concerned, we have only considered the first two stages of the reaction. In the first stage the molecule of carbonic acid is activated by the supply of energy, and in the second stage this activated molecule undergoes atomic re-arrangement, whereby activated molecules of formaldehyde and oxygen are produced. Whereas the oxygen molecule in all probability oxidises a molecule of chlorophyll A to chlorophyll B, the question still remains unanswered as to the future history of the activated formaldehyde molecules. The behaviour of these molecules forms one of the most fascinating features of phytosynthesis, for they are endowed with a very extraordinary reactivity. It might be expected that the third stage of photosynthetic reaction would consist in the loss of energy by the freshly synthesised formaldehyde to give the ordinary stable form. This, however, does not take place at all, but on the contrary the activated formaldehyde proceeds to enter into three different series of reactions, each of which must form an integral part of the phytosynthetic growth of the plant. It was shown by Moore and Webster that aqueous solutions of formaldehyde on exposure to ultra-violet light are polymerised to reducing sugars, but no evidence was given of the nature of these sugars nor of the wave-length of the light required. It has been shown by experiments carried out in Liverpool that the necessary wave-length of the light is $290\mu\mu$, which at once establishes the fact that the polymerisation of the formaldehyde is photochemically distinct from its synthesis. The importance of this observation lies in the conclusion that if ordinary formaldehyde were produced in the plant it would be necessary to consider the mechanism of its photocatalytic activation. Although it has been proved that the polymerisation of formaldehyde can be photocatalysed this is of scientific interest only, because there is no need to postulate such a mechanism in the plant. On exposure to light of wave-length $290\mu\mu$ the formaldehyde molecules absorb energy quanta and are converted into an active phase of high energy content, and it is these molecules which at once undergo polymerisation to sugars, it being well known that formaldehyde in its ordinary form does not polymerise in this way. It has further been proved, and this is a fact of fundamental importance, that the formaldehyde molecules when first produced by photosynthesis exist in the same reactive phase as when they are photochemically activated by the action of light of wave-length $290\mu\mu$ on ordinary formaldehyde. Since the photochemically activated molecules polymerise to sugars, the freshly photosynthesised molecules do the same. This not only explains the absence of ordinary formaldehyde in the growing leaf, but it also eliminates the serious difficulty which would otherwise arise, namely, the necessity of the photocatalytic activation of the ordinary formaldehyde, if such

were produced, as a separate step in the process whereby sugars are synthesised in the plant. In order to avoid unnecessary confusion only one of the three series of reactions characteristic of the reactive phase of formaldehyde has specifically been mentioned, and the remaining two will be discussed below in connection with the synthesis of nitrogen compounds. At this point it is only necessary to emphasise the fact that formaldehyde when freshly formed by photosynthesis or when directly activated by the action of light of wave-length 290$\mu\mu$ on ordinary formaldehyde exhibits identical reactivity. This identity in reactivity has been emphasised, because in an experimental study of the products of photosynthesis it is simpler to deal with photochemically activated formaldehyde than with the photosynthesised material, on account of the greater ease with which the former can be obtained.

The extraordinary reactivity of the activated molecule of formaldehyde suggests that it possesses a different structure from ordinary formaldehyde. The well-known reaction in which carbon monoxide is obtained by the dehydration of formic acid has not as yet been reversed, that is to say, formic acid has not been obtained by the direct union of carbon monoxide and water. The explanation of this is that the carbon monoxide molecule normally exists in a non-reactive phase, and a very large quantity of energy is required to activate it. There is no doubt that the reaction $CO+H_2O=HCO_2H-K$ calories would take place photochemically in the presence of light of very short wave-length ($\lambda=180\mu\mu$), such as is absorbed by carbon monoxide, and hence capable of activating it. The second stage of the reaction would then consist in the formation of activated formic acid

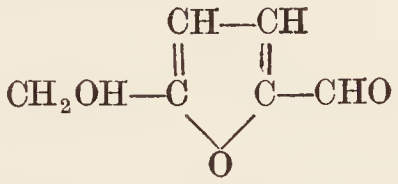
$$C=O+H_2O=C<^{OH}_{OH}+F$$

and the third stage would be the loss of energy and the change in structure to the normal form

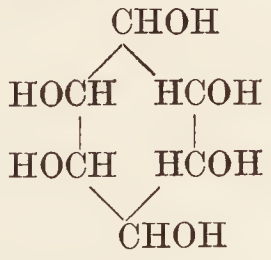
$$C<^{OH}_{OH}=H-C\ll^{O}_{OH}+G$$

The active phase of formic acid therefore would be the true hydrate of carbon monoxide, a derivative of bivalent carbon. By analogy the freshly synthesised or photochemically activated molecule of formaldehyde may be represented by the constitution $C<^{H}_{OH}$, which also is a derivative of bivalent carbon. This formula well explains the great readiness with which it polymerises to sugars of the general formula $(CH_2O)_n$, and it also accounts for the other reactions which this substance undergoes. Indeed it would seem from investigations carried out in Liverpool that the extraordinary reactivity of this substance is one of the most important factors in phytosynthesis.

The discovery of the mechanism of the photochemical process, whereby the plant synthesises formaldehyde, has suggested several lines of investigations, and one of the most important of these is the determination of the nature of the sugars which are produced when the activated formaldehyde undergoes polymerisation. Although Moore and Webster were the first to prove the formation of reducing sugars they were unable to identify them. It is obviously of great importance that these sugars be identified, since on this will depend the explanation of the phytosynthesis of cane sugar and the starches and celluloses in the plant, which must be formed by the condensation together of the photosynthesised sugars. This investigation has been undertaken in Liverpool, and although it is not yet fully complete most promising and suggestive results have already been obtained. By the photochemical activation of ordinary formaldehyde in aqueous solution several hundred grams of concentrated sugar syrup have been prepared. A qualitative analysis of this syrup has shown that the sole products of the polymerisation are hexoses, no trace of a triose or pentose having been detected, and it is perhaps not out of place to draw attention to the delicacy of the test for pentoses. Although the quantitative study of this by methylation and subsequent fractionation is still under investigation, it may be stated that there can be no possible doubt that the sole products of the polymerisation of the photosynthesised formaldehyde in the living plant are also hexoses. This polymerisation to give hexoses only is very striking, in view of the greater possibility on the kinetic theory of the formation of sugars containing less than six carbon atoms, and it leads at once to the conclusion that the determining factor is spatial configuration. Not only does this afford a ready explanation of the storage of starch in the chloroplast during the period of photosynthetic activity and its subsequent hydrolysis to hexoses which are utilised by the plant in later syntheses, it also establishes the fact that the pentoses which are always found in the plant must be formed from the hexoses, possibly through furane compounds, such for instance as ω-hydroxymethylfurfuraldehyde



which is known to be formed very readily from hexoses. It also opens the door to most promising theories of the syntheses of other plant products, every stage of which is most attractive in its simplicity. The most favourable configuration that could possibly be secured by the polymerisation of the activated formaldehyde is the cyclic compound



and, indeed, in view of the formula attributed to the formaldehyde this is the simplest possible result of polymerisation, for it is obvious that if an open chain compound were formed there is nothing to favour a hexose rather than a pentose or a heptose. In suggesting this cyclic compound as being the first product of polymerisation, it must be very definitely stated that this

molecule when first formed is in a state of high energy content and is therefore metastable. It may lose energy in one of three ways to give a stable molecule. In the first place it may lose energy without rupture of the ring to give inosite which frequently occurs in the leaf. In the second place, by wandering of hydrogen atoms and rupture of the ring, it may give the open chain molecule either of glucose or fructose. Each of these by further loss of energy can pass by stages into its ethylene, propylene, or butylene oxide structure. Great emphasis must be laid on the fact that the hexoses are produced by the polymerisation of the photosynthesised formaldehyde in active phases of high energy content. The condensation of a molecule of glucose and a molecule of fructose to give a molecule of cane sugar is therefore a natural consequence, and the failure to realise this reaction in the laboratory is merely due to the fact that as yet no means have been discovered of converting the ordinary hexose molecules into the required phases. Similarly also the formation of starches and celluloses or of glucosides by the condensation of the active hexose molecules together or with other active molecules is possible, and, indeed, some evidence has been found that during the photosynthesis of sugars from formaldehyde in the laboratory a substance of far greater complexity even than cane sugar is simultaneously produced. It is impossible to believe that the phytosynthetic process initiated by the photocatalytic production of active formaldehyde comes to an end when the hexose molecule is formed. Since these are themselves initially produced in highly reactive phases, condensation between them is bound to ensue and the highly condensed molecules of starch or cellulose are the inevitable end products of a whole gamut of condensation reactions in which energy is lost.

Phytosynthesis of nitrogen compounds.—A most important problem in phytosynthesis is the origin and formation of the many complex nitrogen compounds which occur in the plant. On the one hand there are the amino-acids and proteins, and on the other hand there are the nitrogen bases and the alkaloids. Much valuable pioneer work has been carried out by Baudisch (Ber. 1911, 44, 1009; 1913, 46, 115; Zeitsch. angew. Chem. 1913, 26, 612) in his attempts to elucidate this problem, but although many results of great interest were noted by him, he did not succeed in formulating a satisfactory and co-ordinated theory. Some investigations in Liverpool (Baly, Heilbron and Hudson, Chem. Soc. Trans. 1922, 121, 1078), starting from the fact of the highly reactive formaldehyde, have yielded most promising results on which it has been found possible to base a definite theory. There is little doubt that the original source of the nitrogen must be potassium nitrate, calcium nitrate, or, possibly, ammonium salts, and the question to be answered is whether the plant is able from one or both of these sources by the use of activated formaldehyde to synthesise the many complex nitrogenous substances found in the vegetable kingdom. Up to the present two investigations have been carried out, one with potassium nitrate and the other with ammonia, and the results already obtained in each case are of great interest. A passing reference may be made to the fact, first noted by Moore and Webster (Proc. Roy. Soc. 1919, 90 B, 158), that nitrates are readily reduced to nitrites by ultra-violet light, the suggestion being made by these observers that this photochemical change is the first step in the synthesis of the naturally occurring nitrogen compounds. Moore and Webster, however, did not indicate the manner in which the nitrites are utilised in the plant. Although this photochemical observation has been confirmed in Liverpool, it would seem to be of little importance as far as the vital synthesis is concerned, since it is in the highest degree improbable that ultra-violet light can penetrate the highly absorbing cellular tissues of the plant. Further, it has been proved that potassium nitrate is reduced to nitrite within the roots and stems of plants, where obviously no photochemical reaction is possible.

Now it has been shown by Schimper (Bot. Zeit. 1888, 46, 65) that nitrites are always present in the living leaf when the plant is in the dark, and that they disappear when the leaf is exposed to light. Moreover, the disappearance of the nitrites only takes place when chlorophyll is present, since, when a partly etiolated leaf is illuminated, the nitrites remain unaltered in those portions of the leaf which contain no chlorophyll. It has now been found that activated formaldehyde readily combines with potassium nitrite to give formhydroxamic acid, and also that this substance at once reacts with more molecules of activated formaldehyde to produce a great variety of complex substances such as are found in the living plant. This photosynthetic production of formhydroxamic acid was first discovered by Baudisch, who exposed an aqueous solution of potassium nitrite containing methyl alcohol to ultra-violet light. It has also been proved that the reaction takes place between activated formaldehyde and the nitrite by passing carbon dioxide through aqueous solutions of either potassium nitrate or nitrite, which were exposed to ultra-violet light, and also by exposing solutions of the nitrate or nitrite containing formaldehyde to the light. In each case the production of formhydroxamic acid was proved, whilst none was formed when a solution of potassium nitrite and formaldehyde was allowed to remain in the dark even at 100°. It has further been found that no reducing sugars are formed when sufficient nitrite is present to react with all the activated formaldehyde, but that, if the activated formaldehyde is produced in excess of that utilised by the nitrite, reducing sugars are produced. Three important conclusions may be drawn from these facts—

(1) Activated formaldehyde such as is photosynthetically produced reacts with potassium nitrite.

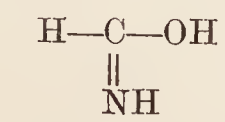
(2) This reaction takes precedence of the polymerisation of the activated formaldehyde to reducing sugars.

(3) When the activated formaldehyde is produced at a rate greater than that at which it can react with the nitrite and with the formhydroxamic acid thus formed, the excess polymerises to reducing sugars. In this case, the two reactions take place simultaneously and independently.

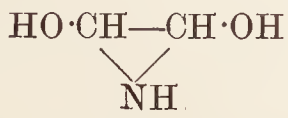
There is no doubt that formhydroxamic acid

marks the first step in the phytosynthesis of the nitrogen compounds found in the plant. This has been proved, not only by the fact that this compound is actually produced by the direct action of activated formaldehyde on potassium nitrite, but also by the fact that formhydroxamic acid reacts with activated formaldehyde to give compounds which are known to occur in the living plant. An aqueous solution of formhydroxamic acid is only very slowly acted on by ultra-violet light, and, further, no change occurs on keeping the solution of the acid and formaldehyde in the dark. If the latter solution is exposed to ultra-violet light both the formhydroxamic acid and the formaldehyde rapidly disappear, the test for sugars always being negative unless the aldehyde is present in excess. Further, by the action of ultra-violet light on an aqueous solution of potassium nitrite and formaldehyde, substances more complex than formhydroxamic acid are formed, although this is the first compound produced. These results therefore explain the observations made by Schimper which were referred to above.

Aqueous solutions of formhydroxamic acid were prepared, and these, after the addition of formaldehyde, were exposed to ultra-violet light. The products formed vary considerably with the relative concentrations of the acid and formaldehyde, and the difficulties are considerably increased by the very remarkable velocity of the reactions. Substances are produced in the first hour, only to give place shortly afterwards to more complex compounds by further condensation with activated formaldehyde. The variations in the results obtained establish the fact that there are at least three ways in which activated formaldehyde can condense with formhydroxamic acid. It may first be recorded that definite proof has been obtained of the formation of α-amino-acids, and, further, in a few experiments methylamine was produced. It was found that the methylamine is synthesised by the action of the activated formaldehyde on ammonia, since ammonia sometimes appears as a secondary decomposition product of formhydroxamic acid. This photosynthesis of methylamine has been abundantly proved by the collateral experiments with ammonia, and is of great interest, since it forms a direct experimental proof of Pictet's contention that in phytosynthesis formaldehyde acts as a methylating agent. Mention may be made of an observation which is of considerable importance with reference to the mechanism of the synthesis of compounds by the action of activated formaldehyde on formhydroxamic acid. In all these reactions oxygen is set free, a fact that is proved by the oxidation of considerable quantities of the formaldehyde to formic acid, a phenomenon which does not occur when aqueous solutions of formaldehyde are exposed to ultra-violet light. This leads to the view that formhydroxamic acid readily loses oxygen and, indeed, that at the moment of its reaction it may be represented as

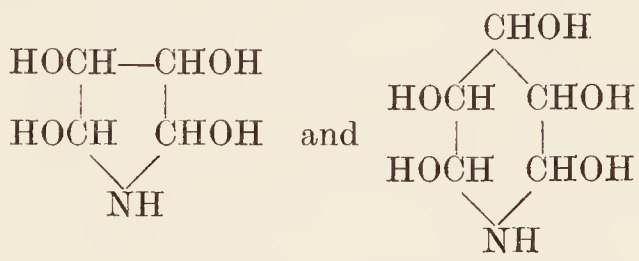


It may be noted that this substance is a hydrate of hydrocyanic acid, a fact which is of importance in connection with the formation of cyanogenetic glucosides. This molecule can react with activated formaldehyde in several ways. In the first place it can combine with one molecule of activated formaldehyde to give the labile ring compound

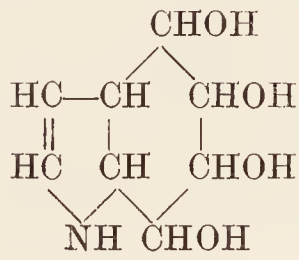


which by re-arrangement will doubtless give glycine. Then, again, since the amino-group is protected by internal salt formation the median CH_2 group of glycine may react with more molecules of activated formaldehyde to give the homologues of glycine. This scheme necessitates that every acid must have the amino-group in the α-position, which, of course, is invariably the case in phytosynthesis. The α-amino-acids have been isolated in the form of their hydrochlorides, but as yet they have not been identified.

Arguing from the spatial configuration which is justified by the hexose synthesis, the two most stable configurations will be the ring compounds formed by the condensation of either three or four molecules of the formaldehyde with one molecule of formhydroxamic acid, namely—



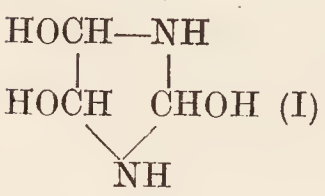
These compounds, by the loss of oxygen and water, will give pyrrolidine or pyrrole compounds and piperidine or pyridine compounds respectively. Then, again, pyrrole and pyridine may condense with more molecules of the activated formaldehyde to give indole compounds on the one hand and quinoline and *iso*-quinoline on the other. For example, in the case of pyrrole the first product of the condensation will be



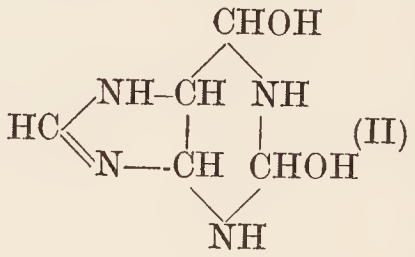
which by the loss of oxygen and water will give indole. The simplicity of these syntheses is peculiarly attractive, for they are the natural result of bringing together potassium nitrite and the activated formaldehyde which is photosynthetically produced from carbonic acid by the photocatalytic agency of the chlorophyll, the condensation resulting in ring formation in each case. They are, moreover, not too speculative, since Baudisch states that he has proved the presence of both pyrrole and pyridine derivatives in solutions of potassium nitrite and methyl alcohol after long exposure to ultra-violet light. In the Liverpool experiments with formhydroxamic acid and formaldehyde evidence has also been obtained of pyridine and piperidine,

but not as yet of pyrrole. As already explained, however, the photosynthesis under these conditions is extraordinarily rapid and very soon goes beyond the formation of simple compounds. If a solution of formhydroxamic acid containing formaldehyde is exposed for twelve hours to the light of the quartz mercury lamp, there is always produced a nitrogen base which is of an alkaloidal nature. At least two different alkaloids have been obtained in this way, one of which is a volatile oil with an odour resembling that of tobacco, whilst the other is a solid of low melting-point with an odour resembling that of burnt feathers. Both form crystalline salts with acids and give strong positive tests with all the usual reagents for alkaloids. It may be noted that the first-mentioned alkaloid is probably identical with that obtained by Baudisch.

There yet remains to be considered another direction along which the condensation of formhydroxamic acid with activated formaldehyde can proceed. Two molecules of formhydroxamic acid can condense with one molecule of the formaldehyde to give the compound I, which by loss of



(I)



(II)

oxygen and water gives glyoxaline. Furthermore, it is possible that a molecule of glyoxaline will condense with two more molecules of formhydroxamic acid to give the compound II, which is a xanthine derivative, and it may be suggested that the phytosynthetic production of xanthine, theobromine, and caffeine follows this course. A considerable amount of experimental evidence has been found in favour of this suggestion, since a solution of formhydroxamic acid containing a little formaldehyde has been found, after illumination for two hours only, to give a nitrogen base which responds to all the tests for glyoxaline. The formation of glyoxaline would remove the suggested phytosynthesis of xanthine from the realms of speculation, and the evidence now obtained establishes considerable confidence in its truth.

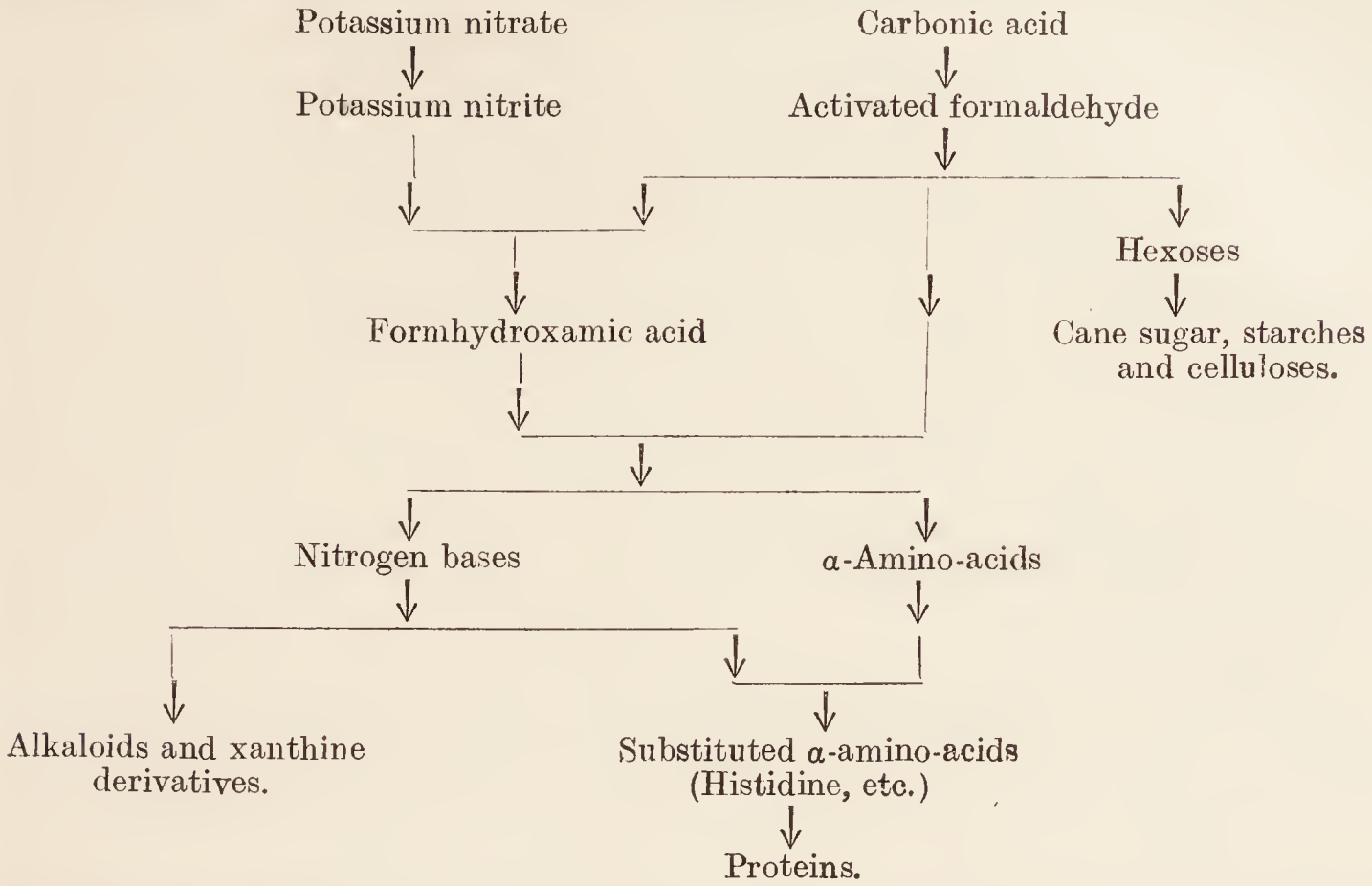
It was stated above that α-amino-acids have been identified amongst the products of the action of activated formaldehyde on potassium nitrite or formhydroxamic acid. Not only is this the case, but more recent work has shown that substituted α-amino-acids are also produced. Very definite evidence has been obtained of the formation of at least one of these complex acids, and, furthermore, the possibility of one of them being histidine is by no means precluded. The formation of histidine would of course materially strengthen the arguments for the formation of glyoxaline and the xanthine synthesis suggested above. The synthesis of a substituted α-amino-acid is undoubtedly a matter of great interest, but once again it is only a natural consequence of the photosynthetic process. The fact that acids of the type of histidine, &c., are readily formed is proved by their occurrence in the living plant. The present results establish the fact that the syntheses of nitrogen bases and of α-amino-acids take place concurrently when formaldehyde is photosynthetically produced in the presence of potassium nitrite. Since both types of compound, when first synthesised, exist in a highly reactive phase, their combination to form substituted α-amino-acids ensues without difficulty. The phytosynthesis of proteins is only one stage further in the process, namely, the inter-condensation of the various substituted amino-acids, again a natural consequence of their existing in highly reactive phases when first synthesised. Although as yet no evidence has been found of protein formation, there is now little doubt of the manner in which these bodies are synthesised in the living plant.

Brief reference may be made to the results of the investigation of the products formed by the interaction between activated formaldehyde and ammonia, for they give very strong support to those already recorded. This investigation was carried out in two ways, by the action of light on solutions of ammonia saturated with carbon dioxide, in which case the active formaldehyde is photosynthesised, and by the action of light on solutions of ammonia and formaldehyde, when the formaldehyde is photochemically activated. It may be stated that in neither case is hexamethylenetetramine formed, and this is not surprising, since this reaction is characteristic of ordinary formaldehyde only. The formation of methylamine has already been dealt with and need not further be discussed. A most important result is the formation of pyridine and piperidine, because this affords conclusive proof of the previously suggested synthesis of these compounds. The fact that they are synthesised from one molecule of ammonia and five molecules of activated formaldehyde instead of from one molecule of formhydroxamic acid and four molecules of the formaldehyde cannot affect the validity of the suggested synthesis. Still more interesting is the fact that in addition to pyridine and piperidine the formation of coniine has apparently been established. The coniine was identified by its reactions with potassium cadmium iodide, by Melzer's test, by its oxidation products, by the melting-point of its picrate, and, especially, by its physiological reaction.

Experiments have also been carried out on the action of activated formaldehyde on calcium nitrate. Formhydroxamic acid and α-amino acids are formed as in the case of potassium nitrate, but it is interesting to note that the nitrogen bases are apparently different from those described above. The importance of this lies in the possible suggestion that the course of the synthesis may be governed by the alkalinity of the solution.

Mention must be made of the essential difference between the conditions in the living plant and those in the laboratory, namely, the control that is present in the one and completely absent in the other. This want of control very materially increases the difficulty of experiments *in vitro*, owing to the number of products which are formed in small quantities. In spite of these difficulties the experimental results now recorded would seem not only clearly to establish the initial stages of the phytosynthesis of nitrogen compounds, but also to indicate the

main lines along which the phytosynthesis proceeds. The following table shows the general scheme which may be put forward with considerable confidence:—



The activated formaldehyde produced by the photocatalytic action of the chlorophyll on carbonic acid combines with potassium nitrite known to be present in the leaves, this reaction taking precedence of all others. The formhydroxamic acid then condenses with more activated formaldehyde, this reaction taking second place in the order of precedence, whilst all excess of the activated formaldehyde polymerises to form hexoses, and these by intercondensation form cane sugar, starches, and celluloses. The interaction of the activated formaldehyde with formhydroxamic acid follows two main lines, the formation of α-amino-acids and of various nitrogen bases. These nitrogen bases consist of different types, namely, pyrrole, pyridine, and glyoxaline, which by further condensation with activated formaldehyde give indole, quinoline, *iso*quinoline, and xanthine derivatives. In cases where such is possible these bases condense with the α-amino-acids to give the substituted α-amino-acids such as histidine, &c. The excess of nitrogen bases undergoes further condensation to give alkaloids, whilst the substituted α-amino-acids interact to give proteins. The readiness with which all these reactions and also the formation of complex carbohydrates take place is due to the cardinal fact that the various compounds are produced in highly reactive phases, analogous to the highly reactive phase of formaldehyde when photosynthetically formed. It is a matter of common knowledge that these reactions must occur in the living plant, and the results obtained in Liverpool show that the key to the problem is the enhanced reactivity of freshly synthesised molecules.

In conclusion there remain to be mentioned some general deductions as to the relation between the observed results of phytosynthesis and the actual growth of the living plant. In the first place there is the fact that in the various stages of the nitrogen synthesis oxygen must be evolved. In this connection it is very interesting to note the presence in the leaves of the enzyme catalyse, which has the power of accelerating the loss of oxygen by various compounds. The loss of oxygen, therefore, in the various stages of the nitrogen synthesis is certainly not antagonistic to the conditions known to exist in the plant. As already stated, the evolution of oxygen in the experimental photosynthesis has been proved by the oxidation of considerable quantities of formaldehyde to formic acid. In the second place, it is an obvious deduction from the foregoing that the region where this synthesis of the nitrogen compounds occurs must necessarily be restricted to the leaves. Since the synthesis of active hexoses is taking place concurrently, the conditions are perfect for the formation of glucosides, and in all probability the products of the nitrogen synthesis are translocated as soluble glucosides to the various parts of the plant.

Finally, emphasis may once again be laid on the very important conclusion that was previously drawn. The carbohydrates, proteins, alkaloids, &c., are the natural and inevitable results of the photosynthesis of formaldehyde in the presence of small amounts of potassium nitrite. Their formation has at times been thought to savour of the mysterious, the mystery being found in the question as to how a plant succeeds in synthesising the very compounds it needs for its existence. The life and growth of a plant consist in the utilisation of the products formed in its leaves. There is no real mystery in the formation of these products, the plant has no choice in the matter, since with the given conditions of chlorophyll, carbonic acid, light energy, and potassium nitrite a photosynthetic process is started which must follow its inevitable path, the maximum escape of energy, and produce starch, cellulose, protein, and alkaloid, which are the final stages of the energy loss. The chemistry of phytosynthesis

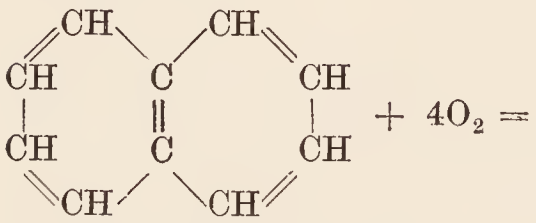
may seem to be new and strange, but it is in the main the chemistry of one single substance, formaldehyde, the chemistry of a formaldehyde endowed with energy and high reactivity by the chlorophyll, which in absorbing light rays acts as the real driving force behind the life and growth of plants. E. C. C. B.; I. M. H.

PHOTOXYLIN (celloidin). Trade name for purified gun-cotton used in photography.

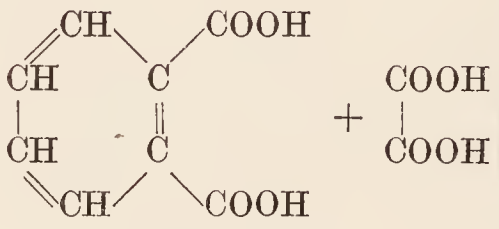
PHTHALEÏN DYES *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PHTHALIC ACID. The three dicarboxylic acids of benzene are known as the phthalic acids. Of these the only one of technical importance is *ortho*phthalic acid $C_6H_4{<}^{COOH\ (1)}_{COOH\ (2)}$, and this is the compound which is always understood when the name *phthalic acid* is used without further qualification, the meta-compound being distinguished as iso*phthalic acid* and the para- as *terephthalic acid.*

*ortho***Phthalic acid** was first obtained by Laurent in 1836 by the oxidation of naphthalene (Annalen, 19, 38), and the same coal-tar product has always served as the chief source of this valuable acid—



Naphthalene.



o-phthalic acid.

Similarly other di-substitution derivatives of benzene containing carbon chains or groups in the ortho- position yield phthalic acid on oxidation, *e.g.* in addition to naphthalene cited above, the three isomeric dimethylbenzenes, tetrachlornaphthalene, alizarin, purpurin, *o*-toluic acid, have been employed, along with such oxidising agents as dilute nitric acid, alkaline permanganate, chromic acid, sulphuric acid (Marignac and others, Annalen, 42, 215; 66, 197; 75, 12, 25; 130, 334; 144, 71; 148, 60; Ber. 6, 945; 7, 1057; 12, 579; 18, 1499; Zeitsch. Chem. [ii.], 4, 551, 705; Compt. rend. 56, 82; Frdl. 1897–1900, 664).

A variety of other methods are known, *e.g.* the action of potassium ferrocyanide and sulphuric acid on salicylic acid, or of formic and sulphuric acids on salicylic acid; interaction of resorcinol and sodium bicarbonate; by the reaction between benzyl chloride, carbon tetrachloride and nitric acid; or by acting upon benzene or benzoic acid with pyrolusite and concentrated sulphuric acid in the cold.

Häussermann (J. 1877, 763, 1158) describes a method suitable for laboratory preparation, from 2 parts of potassium chlorate in 10 parts of commercial hydrochloric acid and 1 part of naphthalene, which mixture is gently heated, chlorination first taking place and then oxidation. The product is washed with water and with light petroleum, and afterwards 10 parts of nitric acid (sp.gr. 1·45) are gradually added and the mixture boiled. When all dissolves, the nitric acid is evaporated and the residue distilled; phthalic anhydride passes over, which may be further purified by sublimation, and reconverted into phthalic acid by boiling with caustic soda and acidifying the cold solution with mineral acid. The precipitated phthalic acid is best purified by recrystallising from boiling water.

Another method consists in passing naphthalene vapours mixed with air or oxygen over a catalyst such as vanadic acid distributed on pumice stone heated to 320°–330°; oxidation to phthalic acid occurs and a white sublimate of phthalic anhydride is formed (Wohl, Eng. Pat. 145071; *cf.* Conover and Gibbs, J. Ind. Eng. Chem. 1922, 14, 120). Phthalic anhydride is obtained by adding 35 kilos. of α-nitronaphthalene to 450 kilos. of conc. sulphuric acid (D 1·82) heated at 150°–160°; when the whole is dissolved 80–90 kilos. of iron borings are stirred in. When the evolution of gas has ceased, the phthalic anhydride is distilled off *in vacuó* at about 300° (Sada, Eng. Pat. 140051).

Physical properties.—It exists in trimetric plates. It melts at 208°±2° (Monroe, J. Ind. Eng. Chem. 1919, 11, 1116), about 195° (Graebe, Ber. 1896, 29, 2806), and decomposes between 196°–199° (Braren, Buchner, Ber. 1901, 34, 995). Sp.gr. 1·585–1·593; 100 parts of water at 14° dissolve 0·54 parts of acid, and at 99° 18 parts of acid (Graebe, Annalen, 1887, 238, 321; *c.f.* McMaster, Bender, and Weil, J. Amer. Chem. Soc. 1921, 43, 1205). Phthalic acid is readily soluble in alcohol, sparingly so in ether and insoluble in chloroform (hence separation from benzoic acid); it is slightly volatile in steam. The acid shows an absorption band in the spectrum, but the anhydride does not. It is said to form a eutectic mixture with its anhydride (de Stadt, Zeitsch. physikal. Chem. 41, 353). For measurements of conductivities reference is made to the work of Jones (Amer. Chem. J. 42, 520; 43, 187; 44, 159); Sidgwick (Chem. Soc. Trans. 1910, 97, 1677); Godlewski (Chem. Zentr. 1904, [ii.] 1275).

Chemical properties.—Phthalic acid forms a characteristic, sparingly soluble barium salt (Carius, Annalen, 1868, 148, 60; Hermann, Annalen, 1874, 171, 78), and also forms salts with most metallic oxides, including bismuth, yttrium (J. pr. Chem. [ii.] 74, 142; Bull. Soc. Chim. [iii.] 31, 135; J. Russ. Phys. Chem. Soc. 42, 586; Ekeley and Banta, J. Amer. Chem. Soc. 1917, 39, 759). The best method of preparing the salts is by acting on the respective carbonates with phthalic acid solution. Calcium phthalate on heating gives benzophenone, benzene, carbon dioxide, small quantities of other hydrocarbons and anthraquinone. The acid itself, when heated with excess of lime, yields benzene and calcium carbonate, calcium benzoate being formed as an intermediate product. The acid is very stable towards sulphuric acid, merely passing into its internal anhydride with loss of water; more strongly heated it loses a little carbon dioxide and is sulphonated. With sulphuric acid it is also said to form a definite additive compound, $C_8H_6O_4+H_2SO_4$ (Hoogewerf

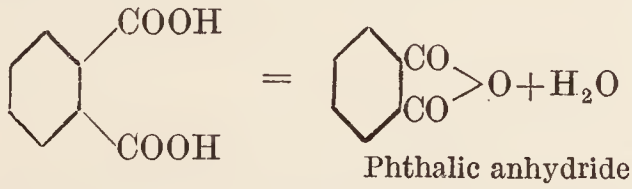
and van Dorp, D. R. P. 21352). Michaelis has prepared a phthalo-arsenic acid

$$(COOH)_2 \cdot C_6H_3 \cdot AsO(OH)_2$$

(Annalen, 320, 271). For other derivatives, *see* Medinger (J. pr. Chem. 1912, 86, 345); Kenner (Proc. Chem. Soc. 1912, 277); Dobbie, Fox and Guage (Proc. Chem. Soc. 1912, 327); Curtius and Semper (Ber. 1913, 46, 1162); Pfeiffer and Halperin (Zeitsch. anorg. Chem. 1914, 87, 335); McCombie and Parkes (Chem. Soc. Trans. 1914, 1690); Kenner and Matthews (*ibid.* 1914, 2476); Lesser and Weiss (Ber. 1913, 46, 3937); Wegscheider and v. Amann (Monatsh. 1915, 36, 549); v. Amann (*ibid.* 1915, 36, 505); Cohen, Woodroffe and Anderson (Chem. Soc. Trans. 1916, 230). Also a number of papers by Pratt and collaborators (J. Amer. Chem. Soc. 1918, vol. 40); Lieb (Monatsh. 1918, 39, 873); Wislicenus and Neber (Annalen, 1919, 418, 274); Csányi (Ber. 1919, 52 [B], 1788).

The *constitution* of the acid has been solved by Nölting (Ber. 1885, 18, 2687) who by oxidising the three xylenes with permanganate obtained excellent yields of the phthalic acids. As meta-xylene forms three isomeric nitro-xylenes, xylidines and xylenols, ortho- two, and para- only one each of these derivatives, therefore *iso*phthalic acid has positions 1, 3, ordinary phthalic 1, 2, and terephthalic 1, 4, for the carboxyl groups.

Phthalic anhydride is formed (1) by distillation of the acid; (2) by warming the acid with acetyl chloride (Laurent, Marignac); (3) by interaction of lead nitrate and phthalyl chloride (Lachowicz, Ber. 1884, 17, 1283); (4) by heating phthalonic acid—itself an oxidation product of naphthalene—to 200°; (5) dissolving the acid in phenol, anisole, or veratrole, containing P_2O_5 (Gazz. chim. ital. 30, ii. 361); (6) shaking a solution of sodium phthalate with two molecules of acetic anhydride (Gazz. chim. ital. 26, ii. 482). All these methods are represented ultimately by the equation—



Phthalic anhydride.

o-Phthalic acid is the only one of the three isomerides which gives in this way an *internal* anhydride. A method of preparation is given by Denham (Chem. Soc. Trans. 1909, 95, 1235) based on the interaction of sulphur monochloride on the sodium salt—

$$C_6H_4(COONa)_2 \rightarrow C_6H_4(COOS)_2 \rightarrow C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O$$

The anhydride forms long, tough needles, m.p. 130·8°, b.p. 284°. Its vapour pressure may be expressed by the formula $\log_{10} p = 7{\cdot}94234 - 2823{\cdot}5/T$, where p is the vapour pressure in mm. of mercury and T the absolute temperature (Monroe, J. Ind. Eng. Chem. 1920, 12, 969). It is very sparingly soluble in cold, more readily so in hot, water, being gradually reconverted into phthalic acid; in alcohol and ether it is readily soluble, and dissolves in alkalis forming phthalates. With dry ammonia it gives phthalimide (*see* below); with alcoholic ammonia phthalamic acid, $C_6H_4(CONH_2)COOH$, m.p. 149°; and with aqueous ammonia it yields ammonium phthalamate $C_6H_4(CONH_2)COONH_4$, which on heating is transformed into phthalimide (*see* later).

Fusion of phthalic anhydride with lime produces benzene and diphenyl (Annalen, 1879, 196, 48); with zinc dust it gives biphthalyl $C_{16}H_8O_4$, or when gradually introduced into a suspension of zinc dust in a solution of calcium chloride in 40 p.c. alcohol at 20°–22° about half is converted into phthalic acid and half into diphenyl-lactonic acid

$$CO{<}\begin{matrix}O\\C_6H_4\end{matrix}{>}CH \cdot CO \cdot C_6H_4 \cdot CO_2H$$

and with zinc dust and methyl iodide yields dimethyl phthalide $C_6H_4{<}\begin{matrix}CMe_2\\CO\end{matrix}{>}O$. In contact with alkaline hydrogen peroxide it reacts with formation of monoperphthalic acid

$$COOH \cdot C_6H_4 \cdot CO \cdot O \cdot OH$$

and the external anhydride of this substance. Three molecules of phthalic anhydride combine with 2 molecules of $SbCl_5$ to form a crystalline compound.

The usual method for the detection of small quantities of phthalic anhydride is that of fusion with about twice the weight of resorcinol in presence of a drop of concentrated sulphuric acid. In this way fluoresceïn is produced (*v. infra*), and the reddish-brown product, when dissolved in dilute caustic soda and poured into a large volume of water, yields a magnificent green fluorescent solution. This reaction is shown by all the ortho-dicarboxylic acids of the benzene series, although with the formation of a variety of coloured solutions, but it is not shown by the meta- or para-dicarboxylic acids. Succinic anhydride shows an analogous reaction.

A method for the quantitative estimation of phthalic anhydride in presence of a number of impurities is described by Boswell (J. Amer. Chem. Soc. 1907, 29, 230). It consists in the careful sublimation of the anhydride and subsequent titration with standardised caustic soda (*cf.* Downs and Stupp, J. Ind. Eng. Chem. 1918, 10, 596).

Technical Manufacture.

Owing to the extensive use of phthalic anhydride in the manufacture of synthetic indigo (*q.v.*) and the pyronine and triphenylmethane class of dye-stuffs, a cheap technical process for its preparation in large quantities was essential, and this has been achieved in the various patents of the Badische Anilin u. Soda Fabrik (*cf.* D. R. P. March 31st, 1896, 91202; Eng. Pat. 18221, August 17th, 1896; Frdl. 1894–1897, 164), which are based upon the observation that naphthalene is readily oxidised by concentrated sulphuric acid containing mercuric sulphate, its oxide, or the metal itself, which acts as a catalyst, and that the sulphur dioxide formed by the reduction of the mineral acid is reconverted into sulphuric acid by absorption of oxygen from the air, the whole process being practically continuous.

In the English patent the quantities given are as follows:—

100	kilograms	naphthalene
1500	,,	sulphuric acid (100 p.c. H_2SO_4)
50	,,	mercuric sulphate.

In place of naphthalene, β-naphthol, naphthionic acid, or phenanthrene may be used. The mercury sulphate remains behind as residue in the retort and is used over and over again.

It should be borne in mind that a too vigorous oxidation will destroy the phthalic acid as soon as formed, and therefore the preparation should be conducted within well-defined limits of temperature—about 270°–300°.

A detailed account of the exact conditions employed, with a description of the manufacturing plant, is as follows.

In a vertical cylinder fitted with a mechanical stirrer, the following substances are mixed, and agitated for three hours until the naphthalene is completely dissolved :—

3675 kilos. sulphuric acid 66°Bé.
1050 ,, oleum (23 p.c. SO_3 content)
350 ,, naphthalene.

The solution (A) so prepared is stored in a reservoir until required.

The oxidation vessel consists of an iron pan, built round with bricks and carefully heated by means of gas jets. The pan possesses a removable lid, has a flat bottom, a diameter of 6 feet, and is 2 feet deep ; a wide tube for leading off the vapours is provided, and through the top passes a shaft connected with a two-arm stirrer, worked mechanically, which just scrapes the bottom of the pan ; also several iron marbles are allowed to rotate on the pan bottom to attract charred matter, and a pressure gauge is inserted on the lid.

The phthalic anhydride sublimes simultaneously with quantities of sulphuric acid which distils over, and these vapours are conducted through a short pipe, 8 inches in diameter, into the condenser, which consists of three concentric lead cylinders fixed one within the other at a distance of about a foot ; two of these communicate with one another through the bottom and open into the third, which is surrounded by an outer condenser, through which water is circulated. The third of these cylinders is again connected with a reservoir into which the condensed sulphuric acid overflows. On the lid of the closed condensers is a vacuum arrangement which conducts off the sulphur dioxide as soon as formed, to an absorption apparatus.

At the beginning of the operation the oxidation pan, containing 120 kilos. of sulphuric acid-monohydrate and 4 kilos. of mercury, is heated for 1½ hours very gently until all the monohydrate distils over, the stirring apparatus being worked during this operation. The prepared solution (A) is now admitted into the pan from a storage reservoir above, in portions of 22 litres, and the gas-heating is so regulated that each 22 litres distils over in about 13–17 minutes. The end of each operation is observed by the increased noise of the rotating marbles on the bottom of the pan, and a further measured lot of 22 litres is then run in.

The process is continued until the pan contains so much charred matter that it is advisable to clean it. The progress of the anhydride formation is controlled by gas analysis, the amount of CO_2 evolved being determined from time to time. When the CO_2 content reaches 0·6–0·8 p.c. the addition of naphthalene solution (A) is discontinued, and in this emergency three times the volume of sulphuric acid of 66°Bé. is admitted and distilled away, after which the vessel is again ready for 2 or 3 days' continuous working. Should the CO_2 gas-content reach 1 p.c., the work is interrupted for a complete cleaning of the vessel ; the pan is heated until perfectly dry, the lid opened, and charred matter chipped from the interior.

To separate the sulphuric acid and phthalic anhydride which together collect in the condenser, the clear sulphuric acid is first decanted, and then the crude phthalic anhydride is further separated centrifugally and washed free from acid. The product is dried and purified by resublimation in a pan mechanically stirred, and heated over a coke fire. A large cylindrical vessel serves as condenser. The cost of this process, as worked in Germany, is about one mark per kilogramme of phthalic anhydride.

Other less well-known methods which may have some technical value for the preparation of phthalic acid are given below.

O. Imray, of the Basle Chemical Works, took out an English patent, No. 15527, on July 31, 1901, for the heating of naphthols in presence of a very slight excess of alkali, with metallic oxides or peroxides, such as copper and iron oxides or barium, lead, or manganese peroxide, to a temperature of about 240°–260°. for 8 hours in oxygen gas under pressure. Phthalic acid and some benzoic acid are formed, together with a few intermediate products (*see* Ber. 1888, 21, 1616). Not only naphthols, but also nitro-naphthalenes, naphthylamines, and naphthalene sulphonic acids may be used (*cf.* D. R. PP. 136410, 138790, 139956, 140999 ; Frdl. 1902–1904, 112–115).

Many patents have been granted for the use of salts of rare earths as catalysts in the oxidation of naphthalene by means of sulphuric acid. The nitrates, oxalates, carbonates, oxyhydrates, sulphates of cerium, lanthanum, neodymium, praseodymium, ytterbium, have all been used as substitutes for the mercury in the original German patent, No. 91202 (*see* above). A mixture of—

25 grms. naphthalene
375 ,, concentrated sulphuric acid
15 ,, oxide of rare earths

evolves gas gently at 100°, and at 200° a vigorous evolution of SO_2 and CO_2 begins and continues briskly until the thermometer registers 270°. Pure white crystals of phthalic anhydride sublime over into the receiver (D. R. PP. 142144, 149677, 152063, 158609). It is claimed that the use of rare earths as a substitute for mercury salts is more economical, as they can always be recovered from the residue in the retort, although the yield is not quite so good as with the use of mercury. A process for the oxidation of naphthalene by electrolysis of a solution of 20 p.c. sulphuric acid and 2 p.c. cerium sulphate is also described (Frdl. 1902–1904, 105–107 ; D. R. P. 152063 ; Gibbs and Conover, Eng. Pats. 119517, 119518).

The observation that naphthalene is partially soluble in boiling water has been utilised by Procházka (Ber. 1897, 30, 3108) for its oxidation to phthalic acid by means of hot permanganate. Almost theoretical results are obtained, phthalonic acid being produced at an intermediate stage. The reduction of permanganate is very

rapid, and the best results are obtained when a large excess of naphthalene is employed, the unchanged hydrocarbon being easily recovered; 100 grms. commercial permanganate yield 17 grms. phthalic acid, the theoretical yield being 19 grms.

The Basler Chem. Fabrik have taken out a patent (D. R. P. 136410; Frdl. 1900–1902, 1301) for the manufacture of phthalic acid together with benzoic acid from α-nitro-naphthalene and nitrophenols by the action of alkalis under pressure and in a dilution medium such as common salt.

Gibbs subjects mixtures of toluene and oxygen or of atmospheric air to contact with various catalysts, *e.g.* oxides of vanadium, or molybdenum, at temperatures varying from the boiling-point of toluene to about 550°, and obtains 82 p.c. yields of phthalic anhydride, free from chlorine and sulphur compounds (J. Soc. Chem. Ind. 1920, 89, 57 R).

Esters of phthalic acid with most of the known alcohols have been prepared in the usual way. Primary alcohols react readily at 100°; secondary alcohols need a temperature above 120°. The dimethyl ester distils at 280°/734 mm.; diethyl ester at 295°; diphenyl ester melts at 73°; benzyl acid ester has m.p. 106°–107°, affording a good characterisation of benzyl alcohol; cyclohexanol acid ester, m.p. 99°, neutral ester m.p. 66°. Various esters of phthalic acid are used as solvents for resins, *e.g.* copal resin, which need not be melted to be dissolved (Hesse, D. R. P. 227667).

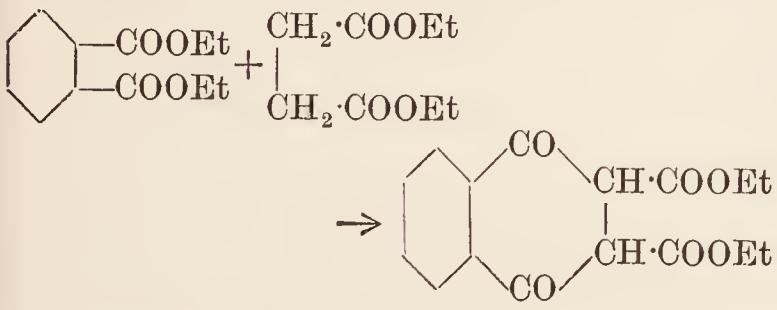
Pickard has accomplished the resolution of various complex alcohols into their optically active components by making the acid-ester by simple fusion with phthalic anhydride and combining this with active bases (Chem. Soc. Trans. 1907, 91, 1974).

The formation of these esters is employed for the separation of alcohols from hydrocarbons, as in the analysis of essential oils. The mixture is heated with phthalic anhydride, treated with sodium carbonate which dissolves the acid phthalate and the latter is then hydrolysed.

Ethyl phthalate reacts with ethyl acetate and sodium to form ethyl diketohydrindene carboxylate; and with ethyl propionate and sodium, yielding methyl diketohydrindene—

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CH\cdot CH_3$$

If ethyl succinate be substituted for ethyl propionate, ethyl dihydronaphthaquinone dicarboxylate is formed.



Derivatives and Condensation Products of Phthalic Anhydride.

The extraordinary reactivity of the anhydride accounts for the great number of important derivatives which have been prepared. First among these should be mentioned *phthalyl chloride*, obtained by the action of phosphorus pentachloride. It is a mixture of two isomerides

$$C_6H_4<\begin{matrix}COCl\\COCl\end{matrix} \text{ and } C_6H_4<\begin{matrix}CCl_2\\CO\end{matrix}>O$$

Sym. chloride. Unsym. chloride.

From this, by the action of ethyl alcohol, the ether $C_6H_4<\begin{matrix}C(OEt)_2\\CO\text{——}\end{matrix}>O$ is obtained, while it also condenses with ketones or with ethyl sodioaceto acetate (Fischer and Koch, Ber. 16, 651; Bülow and Koch, Ber. 1904, 37, 577; 1905, 38, 474). For evidence in favour of the symmetrical structure $C_6H_4(COCl)_2$, *see* Scheiber, Ann. 1912, 389, 121; and also Ott, *ibid.* 392, 245, who has found that on heating phthalyl chloride with aluminium chloride a crystalline isomeride melting at 88°–89° is produced. This form is considered to be the unsymmetrical modification, since it reacts much more slowly with aniline and methyl alcohol. It reverts to the ordinary form on prolonged heating at 100° (*cf.* Copisarow, Chem. Soc. Trans. 1917, 10; Csányi, Monatsh. 1919, 40, 81, for statistics and dynamics of the two phthalyl chlorides). Reduction of phthalyl chloride with zinc and hydrochloric acid produces the important derivative *phthalide* $C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>O$, m.p. 73° (*v.* Lactones), and with acetic acid and sodium amalgam the phthalyl alcohol, $C_6H_4<\begin{matrix}CH_2OH.\\CH_2OH\end{matrix}$

Grignard's reagent acts on phthalic anhydride, forming the dialkyl and diaryl *phthalides*, of which a large variety have been prepared:—

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O+RMgBr$$
$$\rightarrow C_6H_4<\begin{matrix}COOH\\CR_2(OH)\end{matrix} \rightarrow C_6H_4<\begin{matrix}CO\\CR_2\end{matrix}>O$$

(*cf.* Bauer, Ber. 1904, 37, 735; 1905, 38, 240; Arch. Pharm. 247, 220). Pickles and Weizmann (Chem. Soc. Proc. 1904, 20, 201) have prepared *mono*-aryl hydroxyphthalides by this means, which give by the action of water keto acids; anthraquinone has thus been prepared by the following series of reactions:—

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O+MgBrC_6H_5$$
$$\rightarrow C_6H_4<\begin{matrix}C(C_6H_5)(OH)\\CO\text{——}\end{matrix}>O$$
$$\rightarrow C_6H_4<\begin{matrix}CO\cdot C_6H_5\\COOH\end{matrix} \rightarrow C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$$

Simonis and Arand (Ber. 1909, 42, 3721) have succeeded in obtaining acyl benzoic acids by the interaction of Grignard reagents and phthalic acid itself, in addition to the dialkyl phthalides just described, *e.g.* using excess of magnesium ethyl bromide they isolated *o*-carboxy-phenyl ethyl ketone, m.p. 97°, $C_6H_4<\begin{matrix}COC_2H_5.\\COOH\end{matrix}$

Phthalic anhydride condenses with the cresols or their methyl ethers in presence of boric acid or aluminium chloride (*cf.* phthaleïn reaction with phenol):

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O+C_6H_4(CH_3)OCH_3$$
$$\rightarrow C_6H_4<\begin{matrix}CO\cdot C_6H_3(CH_3)OCH_3\\COOH\end{matrix}$$
$$\rightarrow C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2(CH_3)OCH_3$$

(*cf.* Ullmann and Schmidt, Ber. 1919, 52 [B], 2098).

Sulphuric acid effects the closing of the ring in the condensation product, giving oxy-methyl anthraquinones and their methyl derivatives (*v.* METHYL ANTHRACENE; *cf.* Bentley, Gardner, and Weizmann, Chem. Soc. Trans. 1907, 91, 1626; Lambrecht, Ber. 1909, 42, 3591). The simplest case of the above condensation was worked out by Friedel and Crafts, who condensed phthalic anhydride and benzene in presence of aluminium chloride, with the ultimate formation of anthraquinone:—

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle O + C_6H_6 \rightarrow C_6H_4\langle\begin{matrix}CO\cdot C_6H_5\\COOH\end{matrix}$$

$$\rightarrow C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4 + H_2O$$

(*v.* ANTHRAQUINONE, also Friedel and Crafts, Ann. Chim. [vi.] 14, 446; Heller, D. R. P. 193961).

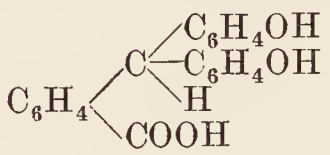
Phthalic anhydride condenses with phenols in presence of a dehydrating agent such as zinc chloride or sulphuric acid, yielding a class of colouring matters known as the *phthaleïns*, which are dealt with in the article on TRIPHENYLMETHANE COLOURING MATTERS. The simplest member of the series is *phenolphthaleïn*, prepared by condensing phthalic anhydride with 2 molecules of phenol (Baeyer, Ber. 1874, 7, 968)—

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle O + 2C_6H_5OH$$

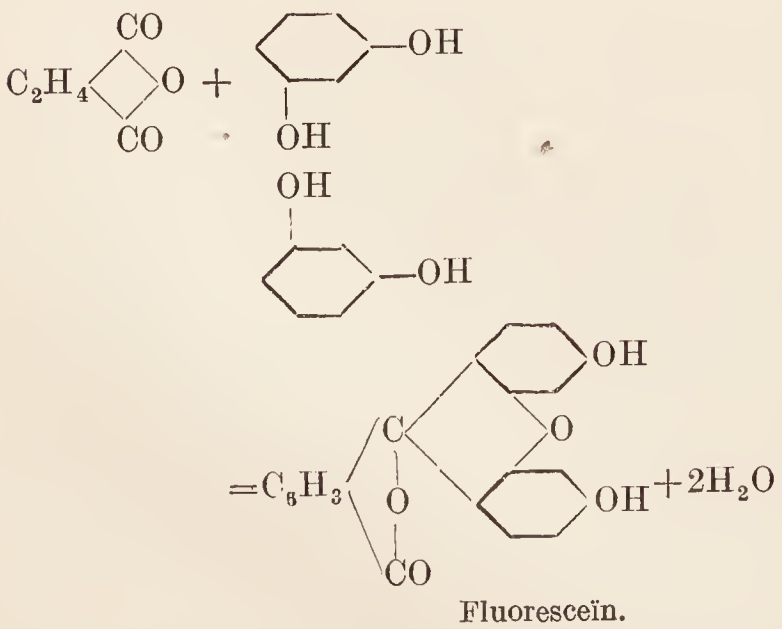
$$= C_6H_4\langle\begin{matrix}C(C_6H_4OH)_2\\CO\text{———}\end{matrix}\rangle O + H_2O$$

Phenolphthaleïn.

On reduction this lactone yields *phthalin*, a hydroxy-derivative of triphenyl methane—



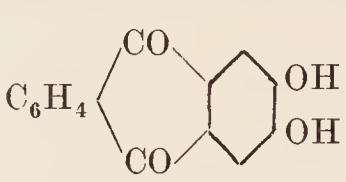
When resorcinol is substituted for phenol the product is the beautiful green fluorescent acid, the sodium salt of which is known in commerce as the dyestuff *uranine*—



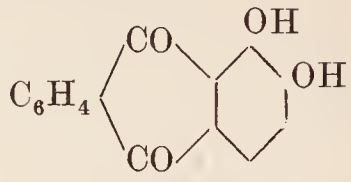
Fluoresceïn.

Eosin is another well-known member of this series of colouring matters, and is a bromo derivative of fluoresceïn.

Catechol condenscs with phthalic anhydridc in presence of concentrated sulphuric acid, with formation of *hystazarin* and *alizarin*:

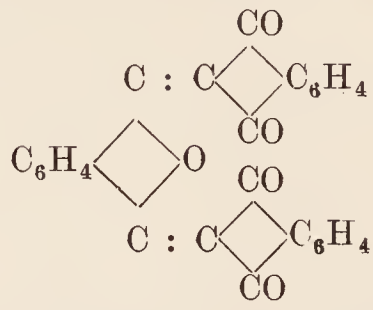


Hystazarin.

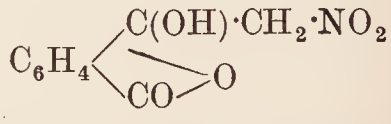


Alizarin.

An interesting condensation is that carried out by Marchese (Gazz. chim. ital. 37, ii. 303). Phthalic anhydride was caused to react with 2 molecules of sodium hydrindene carboxylic ester in presence of acetic anhydride, with the formation of the complex, anhydrophthalo-bisdiketohydrindene, m.p. about 325°—



In many reactions phthalic anhydride shows a similarity to aldehydes. It is attacked by nitromethane in ether solution at 10°, and on adding methyl alcohol and sodium ethoxide, two products are isolated (Gabriel, Ber. 1903, 36, 570)—

$$C_6H_4\langle\begin{matrix}COOMe\\COOH\end{matrix}$$ and 

Again, phthalic anhydride condenses with 1 molecule of α-picolene just as does acetaldehyde or benzaldehyde, yielding in this case *γ-pyrophthalone*—

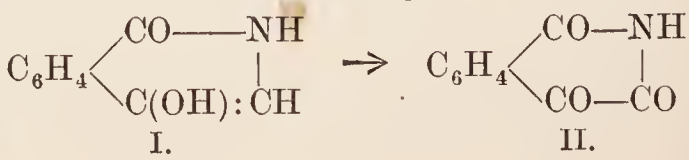
$$C_6H_4\langle\begin{matrix}C(:CH\cdot C_5H_4N)\\CO\text{———}\end{matrix}\rangle O$$

this being known as the 'phthalone reaction' (Düring, Ber. 1905, 38, 161). The same reaction occurs with quinaldine (Eibner, Ber. 1904, 37, 3605) with the lutidines, in some cases using zinc chloride (Scholze, Ber. 1905, 38, 2806; Langer, *ibid.* 3704), with α-methyl indol (Fischer, Annalen, 1887, 242, 381), and with cotarnine (Knoll and Co., D. R. P. 175079).

With *amines* and *amino acids*, phthalic anhydride gives an important series of compounds of the type, $C_6H_4\langle\begin{matrix}CO\cdot NHR\\COOH\end{matrix}$ or the anhydride of this (*cf.* Tingle, J. Amer. Chem. Soc. 1910, 32, 113 and 1319). An example is that of glycine and phthalic anhydride, which give phthalyl glycine

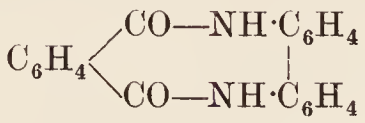
$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle N\cdot CH_2\cdot COOH$$

the ester of which Gabriel and Colman (Ber. 1902, 35, 2534) have converted into an *iso*-quinoline derivative on heating; hydrolysis of this leads to the compound (I.), which with nitric acid yields the interesting substance, phthalonimide (II.), m.p. 224°, a compound obtained also from carbindigo—



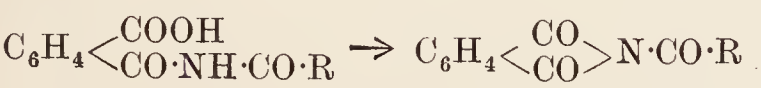
I. II.

Andreasch has prepared in this way the phthalylalanine (m.p. 164°) (Monatsh. 25, 774; *cf.* also Fischer, Ber. 1907, 40, 489; and Annalen, 1888, 248, 152—for taurine). With benzidine the condensation is effected in aqueous solution, giving the compound—



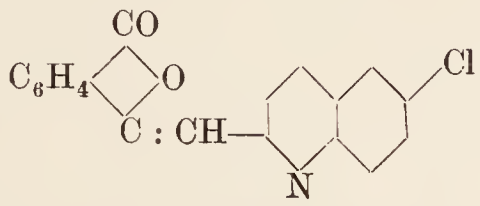
(Koller, Ber. 1904, 37, 2880).

Sodium benzamide or sodium acetamide give the acyl phthalaminic acids (Titherley, Chem. Soc. Trans. 1906, 89, 708), which pass into the acyl phthalimides on dehydration with acetyl chloride—



Some applications of the above reactions to the preparation of dyestuffs are as follows :—

p-Chlor-quinaldine condensed with phthalic anhydride and sulphonation of the quinophthalone so formed—

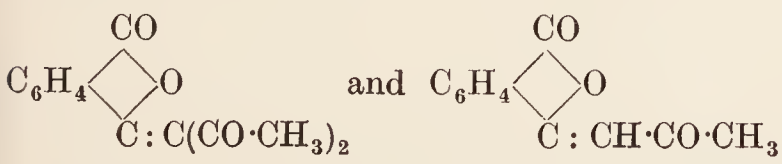


leads to a valuable yellow quinoline dyestuff (Bayer and Co., D. R. P. 204255; Eng. Pat. 1908, 28266; Frdl. 1908–1910, 280).

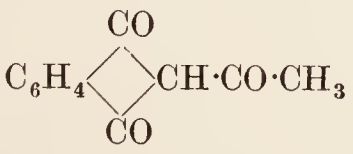
α-Aminoanthraquinone in nitrobenzene condenses with phthalic anhydride in presence of phosphorus pentachloride yielding an orange-yellow dye (D. R. P. 216980); Eng. Pat. 27098, 1901; Frdl. 1908–1910, 753). Dyestuffs of the *acridine series* may be obtained by heating phthalic anhydride with phenylene or toluylene diamines in presence of the hydrochlorides of these bases, with or without a condensation agent such as zinc chloride (D. R. P. 141356; Eng. Pat. 11711, 1902; Frdl. 1902, 1904, 316).

Phthalyl chloride condenses with remarkable ease with substances possessing labile hydrogen atoms, which combine with the chlorine atoms causing the evolution of hydrogen chloride, *e.g.* malonic ester, acetoacetic ester, cyanacetic ester, &c.

Bülow and his collaborators (Ber. 1904, 37, 4379; 1906, 39, 2275) have condensed it with acetyl acetone, and obtained the products—



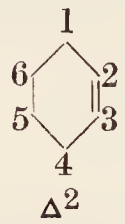
the second of which readily passes into β-acetyl diketo-hydrindene—



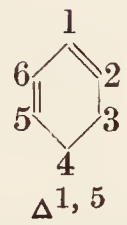
(*cf.* also Eibner, Ber. 1906, 39, 2202).

The Hydrophthalic Acids.

The classical work associated with the name of von Baeyer on the reduction of the phthalic acids has done much to extend our knowledge of valency, and especially of the constitution of the benzene ring. His researches (Annalen, 1873, 166, 346; 1890, 258, 214; 1892, 269, 154) enunciate the general rule that entrance of hydrogen atoms into the molecule undergoing reduction always takes place by attachment first to the α-carbon atoms, *i.e.* those which are adjacent to carboxyl groups. For example, adopting the special nomenclature for the hydrobenzenes, namely—

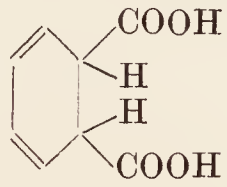


Δ^2



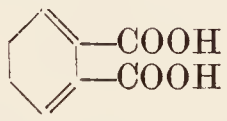
$\Delta^{1,5}$

then the reduction of ortho-phthalic acid with sodium amalgam in weak acetic acid solution, gave rise to the *trans*-$\Delta^{3,5}$-*dihydrophthalic acid*



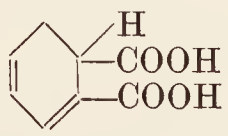
which melts at 210°. This is also prepared by electrolysis of phthalic acid in hot 15 p.c. aqueous sulphuric acid (Mettler, Ber. 1906, 39, 2941). The *cis*-form is only obtained by acting on this with acetic anhydride for 7 minutes, when the *cis-anhydride*, m.p. 100°, is formed, which on boiling with water yields the *cis-acid*, m.p. 175°; prolonged boiling converts the cis- into trans-form. The above $\Delta^{3,5}$-acid is what is known as a $\beta\gamma$ doubly unsaturated acid, the double linkings being both attached to $\beta\gamma$ carbon atoms with reference to the carboxyl groups. This type of acid readily undergoes inversion by digesting with alkalis such as caustic soda, due to the shifting of the double bonds to the $\alpha\beta$ position in each case, so that the compound

$\Delta^{2,6}$-*Dihydrophthalic acid*



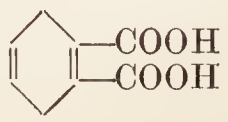
is obtained. This acid is exclusively formed when the reduction of phthalic acid with sodium amalgam is carried out in alkaline solution. It melts at 215°, and its anhydride, formed by the action of acetyl chloride, melts at 84°. Benzoic acid may be obtained from this $\Delta^{2,6}$-acid on oxidation. It is not affected by boiling with aqueous caustic soda, but very concentrated alcoholic potash produces the

$\Delta^{2,4}$-*Dihydrophthalic acid*



which melts at 180°, and which is also obtained indirectly from the dihydrobromide of $\Delta^{2,6}$-dihydrophthalic acid and methyl alcoholic potash. When this $\Delta^{2,4}$-acid is boiled for 6 minutes with acetic anhydride, the anhydride of a new acid

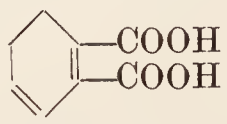
$\Delta^{1,4}$-*Dihydrophthalic acid*



is formed, and on decomposing this with boiling water the above acid is obtained, m.p. 153°. Boiling caustic soda converts it into the $\Delta^{2,4}$ and $\Delta^{2,6}$ isomerides. It may be oxidised back again into phthalic acid. The anhydride of the acid melts at 133°.

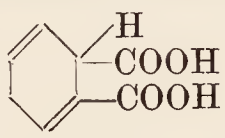
Abati and Bernardinis (Chem. Zentr. 1905, i. 1318) have isolated the two remaining dihydrophthalic acids by a careful scheme for separating the initial reduction products obtained as described by Baeyer. These are the

$\Delta^{1,3}$-*Dihydrophthalic acid*



the *anhydride* of which melts at 59°–60°, and also the

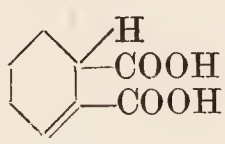
$\Delta^{2,5}$-*Dihydrophthalic Acid*



which is obtained by heating the $\Delta^{1,3}$-acid to 230° in a closed tube; also by the intermediate shifting of the double linking in the $\Delta^{3,5}$-acid by means of caustic soda. Its *anhydride* melts at 73° (*cf.* also Abati, Gazz. chim. ital. 38, i. 152).

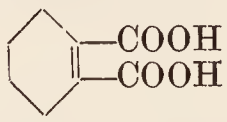
The *Tetrahydrides* are five in number. On reducing a boiling solution of sodium phthalate with sodium amalgam

Δ^{2}-*Tetrahydrophthalic acid*



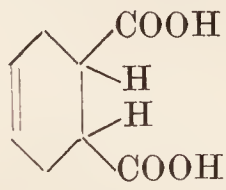
is formed, m.p. 215°; the anhydride melts at 79°, and is made by heating the acid. When this acid is heated for a considerable time at its melting-point, the anhydride of

Δ^{1}-*Tetrahydrophthalic acid*

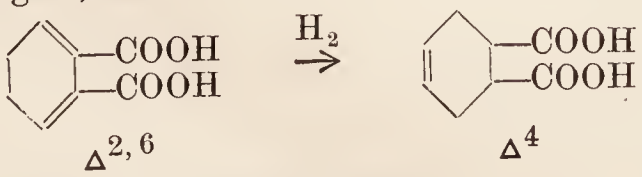


is produced, which on boiling with water gives rise to the above Δ^{1}-acid, m.p. 120°. The *anhydride* melts at 74°. This is also prepared by distilling the tetrahydride of pyromellitic acid. It changes back into the Δ^{2}-acid with concentrated potash, and permanganate oxidises it to adipic acid.

Trans-Δ^{4}-*tetrahydrophthalic acid*



is formed, together with Δ^{2}-acid, by reducing the $\Delta^{2,6}$ dihydride in boiling water with sodium amalgam, that is—

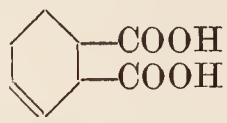


$\Delta^{2,6}$ Δ^{4}

(*cf.* Thiele, Annalen, 1899, 306, 125). This Δ^{4}-acid melts at 218°; its *anhydride*, made by the action of acetyl chloride, melts at 140°, and the *methyl ester* melts at 40°. The acid changes on heating into the *cis-form*, which is also obtained by reducing the $\Delta^{2,4}$-acid at 0° with sodium amalgam. This *cis*-Δ^{4}-acid melts at 174°, and its *anhydride* at 58°.

The remaining isomeride—

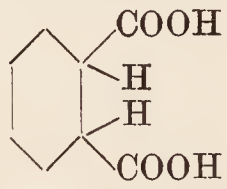
Δ^{3}-*Tetrahydrophthalic acid*



is described by Abati and Vergari (Gazz. chim. ital. 1909, 39, ii. 142). Its *anhydride* melts at 70°–71°.

Both the di- and tetra-hydrophthalic acids are unstable towards permanganate and with milder oxidising agents may be oxidised back to phthalic acid. They form, as a rule, additive compounds with bromine or hydrobromic acid, and yield on reduction hexahydrophthalic acid (*cf.* also Graebe and Born, Annalen, 1867, 142, 330; Astie, Annalen, 258, 187). The physical properties of all these acids have been carefully studied by Abati and his collaborators (Gazz. chim. ital. 39, ii. 142; Chem. Zentr. 1907, i. 886).

Trans-hexahydrophthalic acid



is prepared by reducing all the lower hydrides or their halogen additive compounds, either with sodium amalgam or zinc dust and acetic acid. It melts at 221°, and is not oxidised by cold permanganate. The *anhydride* melts at 140°, and the *dimethyl ester* at 33°. When slowly heated, the acid yields the anhydride of *cis-hexahydrophthalic acid*, from which the free acid is obtained by boiling with water. The acid melts at 192°, and the *anhydride* at 32°.

Nitrogen Derivatives.

Phthalimide $C_6H_4{<}^{CO}_{CO}{>}NH$ is formed by the action of ammonia gas on molten phthalic anhydride, and is a most important stage in the manufacturing process of synthetic indigo.

$$C_6H_4{<}^{CO\cdot ONH_4\ (1)}_{CO\cdot ONH_4\ (2)} = C_6H_4{<}^{CO}_{CO}{>}NH + NH_3 + 2H_2O$$

Ammonium phthalate = Phthalimide.

The method, due to Kuhara, is a quantitative one. Dry ammonia gas compressed in cylinders is used, and is passed into the phthalic anhydride until it ceases to be absorbed, the process occupying in all about 18 hours. The chief condition is that at the end of the operation, when complete transformation of anhydride into -imide has been effected, the mass should remain in the molten state; the anhydride melts at 128° and the imide at 228°, hence during the progress of the operation the temperature should be maintained 1° above the latter. The molten product is run off and allowed to cool and crystallise in open pans; 650 kilos. of anhydride yield 635 kilos. of phthalimide.

Phthalimide may also be prepared by heating

phthalic anhydride with urea (Dunlap, Herzog, Zeitsch. angew. Chem. 1919, 32, 301)

$$2C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle O+NH_2\cdot CO\cdot NH_2$$
$$=2C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle NH+CO_2+H_2O$$

or with aliphatic nitriles (Matthews, J. Amer. Chem. Soc. 1896, 18, 680 ; 1898, 20, 654), or with formamide, acetamide, and other amides, acetanilide, and similar compounds. It forms colourless plates, m.p. 228° (Herzog, 230°–231°), and may be sublimed.

α-Nitronaphthalene is directly oxidised by air or oxygen in presence of a suitable catalyst such as pumice impregnated with an oxide of molybdenum or vanadium, and heated at 300°–400°, the main product of the oxidation being phthalimide in yields of 50 p.c. The operation may be carried out by passing a large excess of hot air over nitronapthalene heated at 120°–130°, and thence through a heated iron tube containing the catalyst (British Dyestuffs Corporation, A. G. Green and S. J. Green, Eng. Pat. 183044).

Reactions.—Amyl alcohol and sodium reduce *phthalimide* to *o*-methyl benzylamine (Bamberger, Ber. 1888, 21, 1888). Distilled with lime, it loses water and carbon dioxide, yielding benzonitrile (Reese, Annalen, 1887, 242, 5). With alcoholic potash it forms a potassium derivative

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle NK$$
$$\downarrow$$
$$C_6H_4\langle\begin{matrix}CONH_2\\COOK\end{matrix}$$

which on boiling with water is converted into potassium phthalamate. Stirred into a suspension of zinc-dust in cold 2N-sodium hydroxide solution, it forms *hydroxyphthalimidine*

$$C_6H_4\langle\begin{matrix}CH(OH)\\—CO—\end{matrix}\rangle NH$$

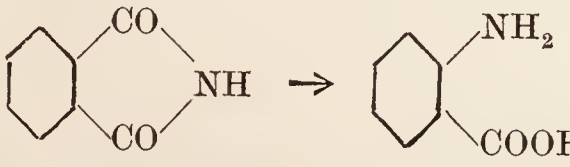
needles, m.p. 171°–172°. On further reduction ammonia is liberated and *phthalide*

$$C_6H_4\langle\begin{matrix}CO\\CH_2\end{matrix}\rangle O$$

is formed in almost quantitative yield (Reissert, Ber. 1913, 46, 1484). On hydrolysis, phthalimide is converted into phthalic acid and ammonia :

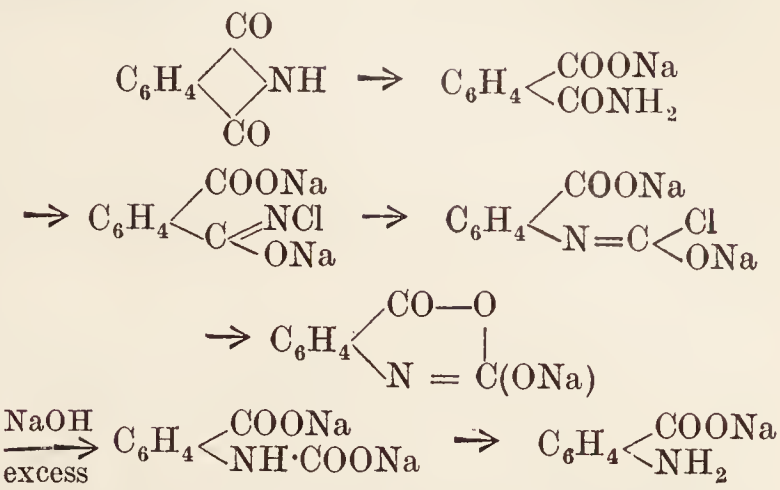
$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle NH+2H_2O = C_6H_4\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}+NH_3$$

From the point of view of indigo its most important reaction is that discovered by Hoggewerff and van Dorp (D. R. P. 55988 , with alkaline KOBr at 80°, when it is trans?ormed into *o*-aminobenzoic acid, or anthranilic acid—

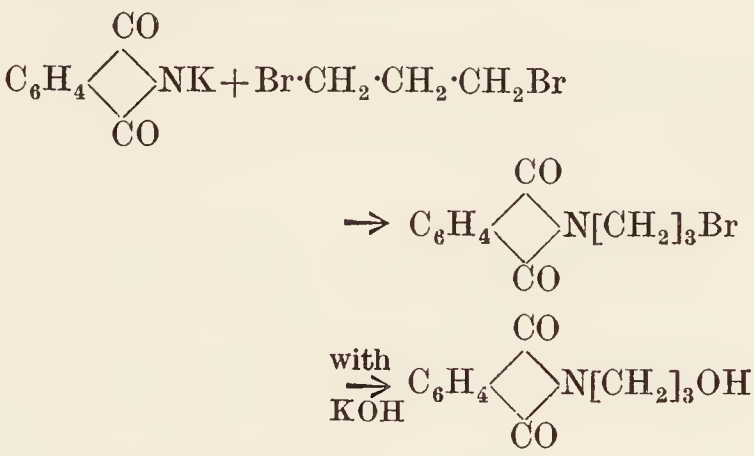


Mohr (J. pr. Chem. [ii.] 80, 1 ; D. R. PP. 127138, 139218 ; Frdl. 1902–1904, 118–120) has modified this by using NaOCl, and states that sodium isatoic acid anhydride is probably formed as an intermediate compound, which

excess of caustic soda converts into sodium anthranilate—

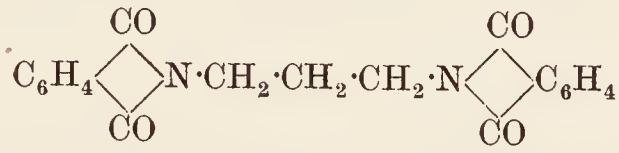


Phthalimide forms a potassium derivative exactly as does malonic ester, in which also the metallic radicle may be substituted for alkyl by contact with halogen compounds (*see resumé* by Sörensen, Zeitsch. physikal. Chem. 44, 448 ; Chem. Zentr. 1905, ii. 401 ; *cf.* also Bull. Soc. chim. 33, 1042). Gabriel describes an interesting example of this use of potassium phthalimide with dibromopropane—



(Ber. 1905, 38, 2389).

Two molecules of phthalimide may also combine with the halogen derivative, giving



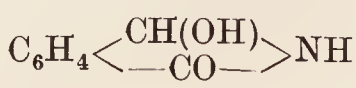
and this on hydrolysis with mineral acids yields trimethylene diamine and 2 molecules of phthalic acid, thus providing an excellent general method for the preparation of diamines.

Various mercaptan derivatives of phthalimide have been prepared by Manasse (Ber. 1902, 35, 1367). Heated with phosphorus pentasulphide in xylene solution it forms dithiophthalimide $C_6H_4\langle\begin{matrix}CS\\CS\end{matrix}\rangle NH$, red needles, m.p. 180°.

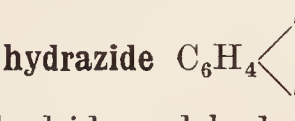
The German patent No. 139553 describes the preparation of *phthal-chlorimide* by leading chlorine into an aqueous suspension of phthalimide (*cf.* Moore, Marrack and Proud, Chem. Soc. Trans. 1921, 119, 1786).

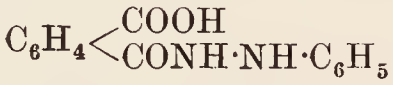
A 40 p.c. solution of formaldehyde gives with phthalimide a methyl phthalimide of m.p. 132° (Breslauer and Pictet, Ber. 1907, 40, 3784). Various Grignard reagents have been tried with success upon phthalimide (*cf.* Béis, Compt. rend. 138, 987 ; Sachs and Ludwig, Ber. 1904, 37, 385). With tin and hydrochloric acid it is reduced to phthalimidine $C_6H_4\langle\begin{matrix}CH_2\\CO\end{matrix}\rangle NH$ (Graebe, Ber. 1884, 17, 2598 ; Annalen, 1888, 247291).

When phthalimide is reduced at the ordinary temperature by means of zinc dust and alkali hydroxide solution *hydroxyphthalimidine*

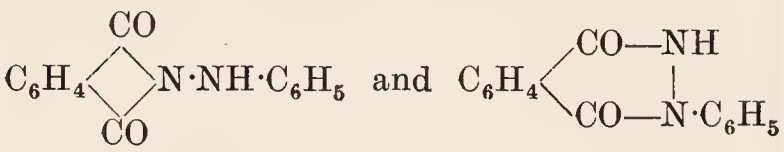


is formed. When the solution is heated the imino group is replaced by oxygen, and the hydroxyl group by hydrogen, *phthalide* being produced.

Phthalyl hydrazide  is made from the anhydride and hydrazine (Curtius, J. pr. Chem. [ii.] 51, 376). The phenyl hydrazine derivatives exists in two forms ; the first product of the condensation is probably a simple additive compound—



which splits off water in two ways, giving—

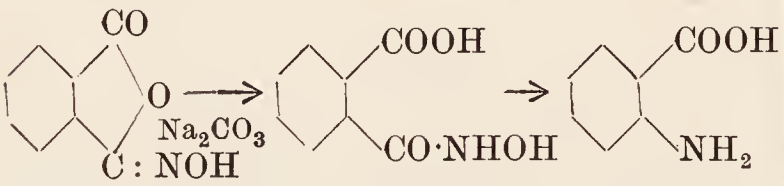


α Phthalyl phenylhydrazine, m.p. 179°. β form.

(Dunlap, J. Amer. Chem. Soc. 1905, 27, 1091 ; Chattaway and Tesh. Chem. Soc. Trans. 1920, 711).

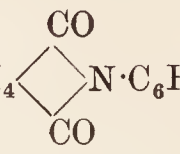
Phthalyl semicarbazide melts at 262°.

Phthalylhydroxylamine. Hydroxylamine condenses with phthalic anhydride in aqueous dilute alcoholic solution or in caustic soda, with formation of phthalylhydroxylamine, m.p. 204°–206° in good yields (Basler Chemische Fabrik, D. R. PP. 130680, 130681). Treatment of the hydrochloride of this with sodium carbonate, and subsequent action of caustic soda, leads to the formation of anthranilic acid—

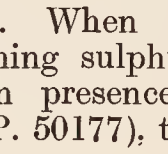


(D. R. P. 136788 ; Frdl. 1902–1904, 117).

Orndorff and Pratt (Amer. Chem. J. 1912, 47, 89) describe two oximes of phthalic anhydride, one colourless, the other yellow, the two being mutually interconvertible. Both yield red solutions in alkali, and are considered to be stereo-isomerides.

Phthalanil  m.p. 205°, is formed by heating 1 molecule of sodium phthalate and 2 molecules of aniline hydrochloride in a closed tube for 6 hours at 200° (J. Amer. Chem. Soc. 1903, 25, 612).

For derivatives *see* Bogert and Wise (J. Amer. Chem. Soc. 1912, 34, 693) ; Chattaway and Constable (Chem. Soc. Trans. 1914, 127) ; Pratt and Young (J. Amer. Chem. Soc. 1918, 40, 1415) ; Pratt and Perkins (*ibid.* 1918, 40, 214, 219) ; Pratt and Miller (*ibid.* 1918, 40, 407) ; Pratt and Downey (*ibid.* 1918, 40, 412) ; *m*-hydroxyphthalanil, m.p. 220 ; *p*-hydroxy-phthalanil, m.p. 250° (Medinger, J. pr. Chem. 1912, [ii.] 86, 345).

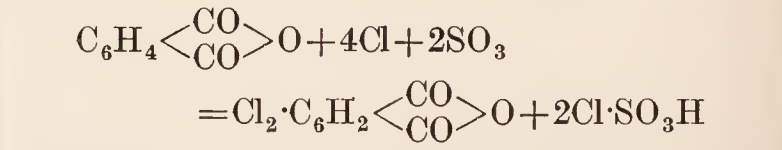
***iso*Phthalanil**  is slowly converted at the ordinary temperature into phthalanil ; more rapidly by treatment with strong solution of sodium carbonate.

Phthalonitrile $C_6H_4<^{CN}_{CN}$ is obtained from 2-aminobenzonitrile by conversion of the NH_2 group into CN (Pinnow and Sämann, Ber. 1896, 29, 630) ; and from *o*-cyanobenzaldoxim by dehydration in contact with acetic anhydride (Posner, Ber. 1897, 30, 1698). It forms odourless needles, m.p. 142°, distils without decomposition, and is volatile in steam. It is transformed into phthalic acid on hydrolysis with concentrated hydrochloric acid.

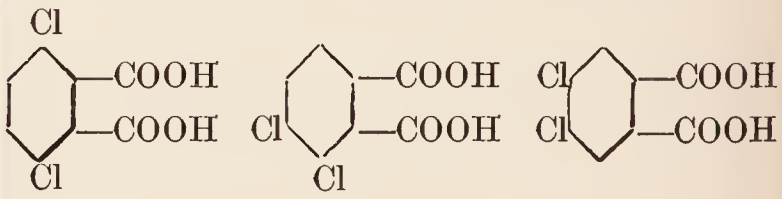
Seminitrile of Phthalic acid $C_6H_4<^{CN}_{COOH}$ (*o*-cyanobenzoic acid) is prepared from anthranilic acid by the Sandmeyer reaction (Ber. 1885, 18, 1499) ; by the action of NH_3 upon phthalyl chloride (Hoogewerff and van Dorp, Rec. trav. chim. 11, 91 ; *cf.* Kuhara, Amer. Chem. J. 3, 26 ; Auger, Ann. Chim. [vi.] 22, 289) ; and from benzaldehydeoxime-carboxylic acid by contact with acetic anhydride. It forms needles melting at 180°–190° and changing simultaneously into phthalimide. Heating with water produces acid ammonium phthalate. The *methyl ester* melts at 51°, and the *ethyl ester* at 70°.

Substituted Phthalic Acids.

Many *chloro, bromo, nitro, sulpho* substituted phthalic acids are known, and references to these are to be found in Beilstein's Handbuch der Organischen Chemie, vol. ii. and its supplement ; also Frdl. 1887–1890, 93 ; Villiger, Ber. 1909, 42, 3529. When phthalic anhydride, dissolved in fuming sulphuric acid, is treated with chlorine in presence of a little iodine (Juvalta, D. R. P. 50177), the following reaction occurs :—



Separation of the products is possible owing to a difference in solubility of the zinc salts, by a recrystallisation of which three isomerides are separated. The chief product is 3 : 6-*dichlorophthalic acid* (I.), smaller quantities of 3 : 4 (II.) and very little of 4 : 5 (III.), being isolated—



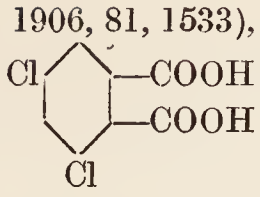
I. II. III.

The 3 : 6 acid has m.p. 253°–258° ; and its anhydride, m.p. 339°.

These acids are more soluble in water and ether than ordinary phthalic acid, and the anhydrides can be distilled (*cf.* also Graebe, Ber. 1900, 33, 2019 ; Pratt and Perkins, J. Amer. Chem. Soc. 1918, 40, 216).

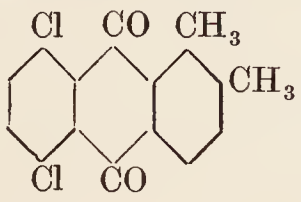
A fourth isomeride is described by Crossley

and Le Sueur (Chem. Soc. Trans. 1906, 81, 1533), viz. the 3 : 5-*dichlorophthalic acid*



(*cf.* also Claus. Ber. 18, 1370; 19, 3175; J. pr. Chem. [ii.] 43, 253, 582; Le Royer, Annalen, 1887, 238, 350).

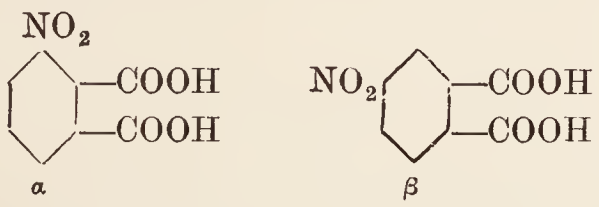
3 : 6-*dichlorophthalic anhydride*, which is now a commercial product, has been condensed with the three xylenes and the closing of the ring effected, with formation of dichloro-dimethyl-anthraquinones (Harrop, Norris and Weizmann, Chem. Soc. Trans. 1909, 95, 1312)—



Tetrachlorophthalic acid is obtained in the form of its anhydride by heating phthalic anhydride with oleum in the presence of a small quantity of iodine and leading chlorine into the mixture at 50°–60°. The temperature is then gradually raised to 200° (Juvalta, D. R. P. 50177). The anhydride melts at 252°.

Of the four possible *dibromophthalic acids* only the *para* (3 : 6-), m.p. 135°, is at present made, the yield being 30 p.c.; 100 grams of dibromo-naphthalene is strongly heated for 2 hours with 2 litres of nitric acid (sp.gr. 1·4); first a nitrated product is obtained, and then on evaporation of the mother liquors to one-third the volume, white crystals of the 3 : 6-*dibromo-phthalic acid* appear (Severin, Chem. Zentr. 1907, i. 1119).

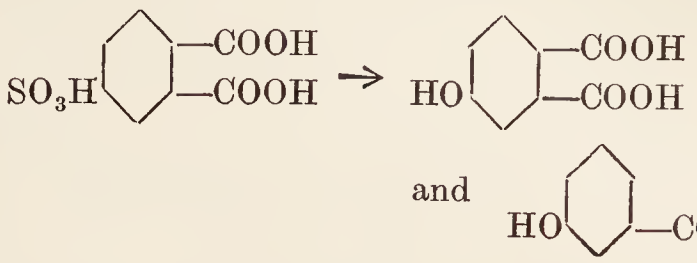
Nitro-phthalic acid. Holleman (Chem. Zentr. 1908, ii. 2011) has studied quantitatively the action of concentrated nitric acid on phthalic acid at 30°, and has found that the product contains 49·5 p.c. of the α- and 50·5 p.c. of the *β-nitrophthalic acid*—



Sulpho-phthalic acids. The Badische Anilin und Soda Fabrik has obtained an English patent (J. Y. Johnson, No. 18221, August 17, 1896) for the preparation of a disulphonic acid. 100 kilos. of naphthalene is dissolved in 300 kilos. of fuming sulphuric acid (23 p.c. SO_3) and mixed with 1200 kilos. concentrated sulphuric acid (95 p.c.). The mass is heated for 10 hours at about 250°; a certain amount of phthalic acid distils over during the reaction. The product is neutralised with calcium or barium carbonate and worked up in the usual way. The new *disulphonic acid* of phthalic acid may be separated from water in crystalline nodules in the form of its barium salt.

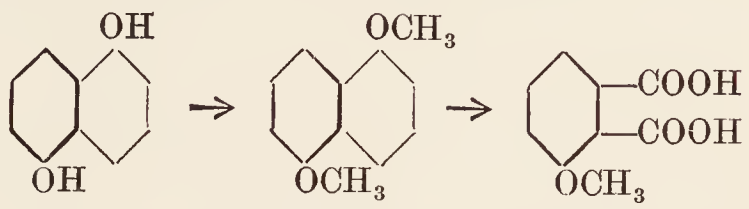
If the temperature is maintained at about 220°, a *monosulphonate* of phthalic acid is obtained.

Hydroxy-phthalic acids. Bentley and Weizmann (Chem. Soc. Trans. 1907, 91, 98) have sulphonated phthalic anhydride with fuming sulphuric acid (73 p.c. SO_3) at 200° and fused the products with caustic soda, obtaining in this way 4-*hydroxy-phthalic acid*, and as by-product *m*-hydroxybenzoic acid—



4-*hydroxy-phthalic acid* melts at 204°–205°, its anhydride at 171°–173°; the *methoxy acid* at 178° and the anhydride of this at 98°.

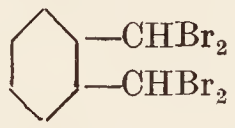
The same authors, with Miss Rona Robinson (Chem. Soc. Trans. 1907, 91, 104), prepared 1 : 5-*di-methoxy-naphthalene* and oxidised this with permanganate, obtaining 3-*methoxy-phthalic acid*, m.p. 173°, the *anhydride* of which melts at 160°—



Fusion of the methoxy acid with caustic potash gives rise to the 3-*hydroxy-phthalic acid*, m.p. 150°—



Phthalaldehyde $C_6H_4{<}^{CHO}_{CHO}$. When *o*-xylene is brominated it yields the tetrabromide



If 400 grams of this bromide are heated with 360 grams of finely powdered crystalline potassium oxalate in an oil-bath for 40 hours, in contact with 2½ litres of water and 2½ litres of 95 p.c. ethyl alcohol, a clear yellow solution results, with evolution of some carbon monoxide and dioxide. After distilling off 2 litres of alcohol, which is used again subsequently, 700 grams of crystalline sodium phosphate are added, and the mass is subjected to distillation in steam, which drives over the phthalic aldehyde. The product is readily soluble in water, and therefore the distillate is extracted several times with acetic ester, which dissolves out the aldehyde, a 90 p.c. yield being obtained in the form of yellow needles, m.p. 56° (Thiele and Günther, Annalen, 1906, 347, 106).

Strong alkali converts phthalaldehyde into phthalide, which appears to be an intramolecular change into a more stable isomeride—



It is interesting to compare this with the 'lactone tautomerism' of aldehydo phthalic acid and hydroxy phthalide, which can react in either form—

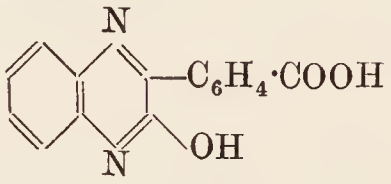


Phthalaldehyde condenses readily with a large number of substances by virtue of its two —CHO groupings; *e.g.* with acetone it yields β-acetyl hydrindone (Thiele and Falk, Annalen, 1906, 347, 112; 1909, 369, 287)—

$$C_6H_4<^{CHO}_{CHO}+CH_3\cdot CO\cdot CH_3$$
$$=C_6H_4<^{CH_2}_{CO}>CH\cdot CO\cdot CH_3+H_2O$$

Phthalonic acid $C_6H_4<^{COOH}_{CO\cdot COOH}$ m.p. 144°–145°, is formed at an intermediate stage of the oxidation of naphthalene to phthalic acid, especially when the reagent used is permanganate (Annalen, 1887, 240, 142; Daly, J. Phys. Chem. 11, 93). It is also produced by the action of nitric acid on tetrachlor-ketohydrindene (Zinke and Fries, Annalen, 1904, 334, 342). Its *acid methyl ester* melts at 79°–81°, and its neutral *methyl ester* at 66°–68° (*cf.* Frdl. 1894–1897, 162–163; D. R. PP. 79693, 86914 (Tcherniac)).

Phthalonic acid takes part in numerous reactions, principally those involving the keto group; *e.g.* it condenses with *o*-phenylene diamin (Gazz. chim. ital. 1904, 34, i. 493), giving the compound—



it gives a phenylhydrazone, m.p. 171°–172° (Mitter and Sen. Chem. Soc. Trans. 1919, 1147). A warm sodium bisulphite solution of sodium phthalonate gives on evaporation and subsequent treatment with hydrochloric acid, *aldehydo-phthalic acid* (Wegscheider and Bondi, Monatsh. 26, 1039).

$$C_6H_4<^{CO\cdot COOH}_{COOH}\rightarrow C_6H_4<^{CHO}_{COOH}+CO_2$$

The following is the best method of preparing phthalonic acid: 10 grams naphthalene is dissolved in 1 litre of water and 90 grams pure $KMnO_4$, or its equivalent of the commercial permanganate, is added, and the whole boiled until the solution is completely decolorised. The removal of the excess of naphthalene (2·5 grams) is effected by steam distillation, the oxide of manganese is filtered off, and the filtrate evaporated and then acidified and the product extracted or allowed to crystallise. The yield is 9 grams of phthalonic acid and 1 gram of phthalic acid.

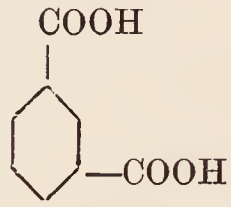
For details and derivatives, *see* Tcherniac, (Chem. Soc. Trans. 1916, 1236); Graebe and Trümpy (Ber. 1898, 31, 369).

Phthalonic anhydride $C_6H_4<^{CO\cdot CO}_{CO\cdot O}>O$, formed by the action of acetic anhydride on phthalonic acid. White or slightly yellow needles. Soluble in boiling ethyl acetate; sparingly soluble in ether, m.p. 185°–186°. With ammonia forms *phthalonamic acid* $NH_2\cdot CO\cdot CO\cdot C_6H_4\cdot CO_2H$ prisms, very soluble in water, m.p. 155° (decomp.). Yields no isatin with alkaline hypochlorite. The phthalonamic acid of Gabriel and Colman (Ber. 1900, 33, 999) has the constitution

$$NH_2\cdot CO\cdot C_6H_4\cdot CO\cdot CO_2H$$

as it yields isatin on treatment with hypochlorite. It melts with decomposition at 178°–179° (Tcherniac, *l.c.*).

*iso***Phthalic acid** (meta-phthalic acid)



is prepared by the oxidation of *m*-xylene with permanganate (Nölting, Ber. 1885, 18, 2687) or with chromic acid (Fitting and Velguth, Annalen, 1868, 148, 11; 1870, 153, 268); or by converting *m*-xylene into the dibromide by bromination at 125°, treating this with hot alcoholic potash, and oxidising the resulting ether with chromic acid mixture (Kipping, Ber. 1888, 21, 46). It is also obtained by fusing potassium formate with potassium benzoate (Richter, Ber. 1873, 6, 876), or with potassium *m*-brombenzoate (Ador and Meyer, Annalen, 1871, 159, 16), or with benzene disulphonic acid (Barth and Senhofer, Annalen, 1871, 159, 228); and by the action of a hot solution of cuprous potassium cyanide on *m*-diazobenzoic chloride and saponification of the resulting nitrile (Sandmeyer, Ber. 1885, 18, 1498).

It forms long slender needles when crystallised from water, which melt at about 300° and which may be sublimed, without, however, forming the corresponding anhydride.

The *dimethyl ester* melts at 67°–68° (Baeyer, Ber. 1898, 31, 1404), and the *diethyl ester* at 11·5° (*cf.* Perkin, Chem. Soc. Trans. 1896, 69, 1238, for physical properties).

It forms a *hydrazide*, m.p. 220°, by heating with hydrazine hydrate in absolute alcohol (Davids, J. pr. Chem. [ii.] 54, 74), and also an *azide*, $C_6H_4(CON_3)_2$.

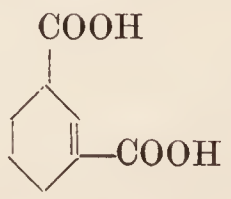
For other derivatives, *see* Meyer (Monatsh. 1920, 41, 125); Axer (*ibid.* 1920, 41, 153); James, Kenner and Stubbings (Chem. Soc. Trans. 1920, 774).

Hydro-isophthalic Acids.

These acids are chiefly due to the work of Perkin and Pickles (Chem. Soc. Trans. 1905, 87, 293) and Perkin and Goodwin (*ibid.* 843).

The *dihydro-isophthalic acids* are not well known. The $\Delta^{1,4}$-acid, m.p. 270°, has been obtained from 1 : 3-dibromo-trans-hexahydro-*iso*phthalic acid by the agency of potash; and the $\Delta^{2,4}$-*dihydro-acid*, m.p. 255°, is also described as obtained in a similar manner from the 3 : 4-dibromohexahydro acid, but the constitution of these two acids is still regarded as unsettled.

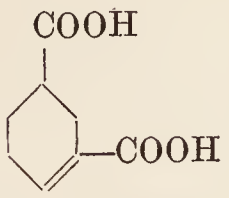
All the four possible *tetrahydro acids* have been isolated. *iso*-Phthalic acid on reduction with sodium amalgam yields two acids, Δ_2 and the cis-form of Δ_4. Δ^2-*Tetrahydro-isophthalic acid*



melts at 168°, is very soluble in water, and its anhydride melts at 78°. By the agency of caustic potash or

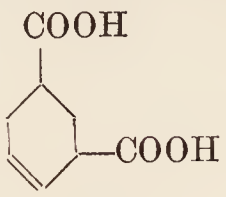
hydrochloric acid it yields the sparingly soluble

Δ^3-*tetrahydroisophthalic acid*



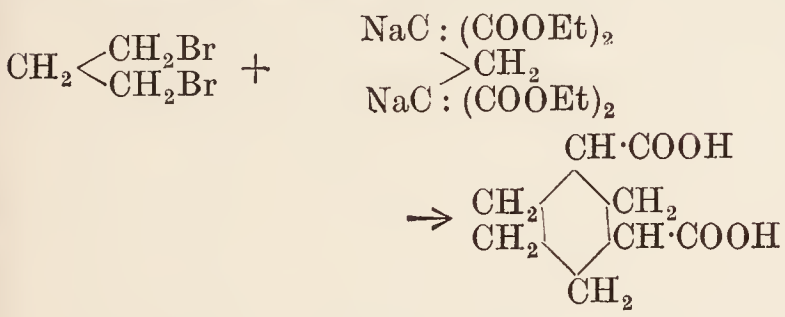
m.p. 244°, which gives, with acetic anhydride, the anhydride of Δ^2-acid, m.p. 78°.

Cis-Δ^4-*tetrahydroisophthalic acid*



is isolated from the original reduction product, as stated above. It melts at 165°, is very soluble in water, and is easily converted into the *trans-acid* with concentrated hydrochloric acid. This trans-form is sparingly soluble, and melts at 227°.

Cis- and *trans-hexahydroisophthalic acids*, m.p. 163° and 148° respectively, were obtained synthetically by Perkin and Prentice (Chem. Soc. Trans. 1891, 59, 808; *cf.*, however, Perkin and Goodwin, Chem. Soc. Trans. 1905, 87, 843), who condensed trimethylene bromide with sodio-methylene-malonic ester—



The tetrabasic ester first formed yielded on hydrolysis a mixture of cis- and trans-hexahydro-*iso*phthalic acids. Baeyer and Villiger were able to verify these results by the actual reduction of *iso*phthalic acid (Annalen, 1893, 276, 255).

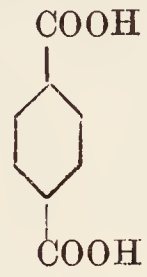
5-Chloro-*iso*phthalic acid is prepared by the oxidation of 5-chloro-*m*-toluic acid with alkaline permanganate (Klages, Knoevenagel, Ber. 1895, 28, 2045); and *tetra-chlor* and *tetra-brom* derivatives are prepared by oxidation of the correspondingly substituted xylenes (Rupp, Ber. 1896, 29, 1631).

2-Nitro- and **4-nitro-*iso*phthalic** acids have been prepared by Holleman (Rec. trav. chim. 27, 260; Chem. Zentr. 1908, ii. 2011) by oxidising the corresponding nitro-*m*-xylenes with alkaline permanganate. Direct nitration of *iso*phthalic acid with concentrated nitric acid at 30° was found to give 97 p.c. 5-nitro- and 3 p.c. 4-nitro-*iso*phthalic acids. The 2-nitro- and 4-nitro-*iso*phthalic acids melt at 300° and 245° respectively.

***iso*Phthalaldehyde** is prepared in theoretical yields from ω-tetrabromo-*m*-xylene by boiling with potassium oxalate in aqueous alcohol. It melts at 89·5° and forms colourless silky needles. The dioxide melts at 180° (Thiele and Günther, Annalen, 1906, 347, 109). Forms 4 : 6 dichloro-*iso*phthalaldehyde, m.p. 163° (D. R. P. 243749).

***iso*Phthalaldehyde acid.** *Iso*phthalaldehyde heated with bromine under pressure yields the acid bromide of *iso*phthalaldehydic acid, which by internal condensation forms monobromo phthalide. On hydrolysis this forms *iso*-phthalaldehydic acid. Colourless needles, m.p. 175°. The *methyl ester*, m.p. 53°, forms an *oxime*, m.p. 104°; the *ethyl ester* is a colourless liquid, b.p. 278°, m.p. −10°, D^{18} 1·093. For other derivatives *see* Simonis, Bochme and Benenson (Ber. 1912, 45, 1584).

Terephthalic acid (*para*-phthalic acid)—



is formed by the oxidation of most derivatives of benzene having carbon chains in the *para* position, *e.g.* the terpenes, *para*-xylene, *p*-toluic acid, &c., and by the analogous methods given under *iso*phthalic acid, such as the fusion of *p*-disulphobenzene with sodium formate (Romsen, Ber. 1872, 5, 379). It may be prepared by von Baeyer's method (Annalen 1888, 245, 139), from dibromo-*p*-xylene, $C_6H_4(CH_2Br)_2$, by digestion with potassium acetate in absolute alcohol, and subsequent oxidation of the acetate, $C_6H_4(CH_2O{\cdot}OCCH_3)_2$, with alkaline permanganate; or by the method of Beilstein (Annalen, 1865, 133, 41), in which *p*-xylene is oxidised with chromic acid mixture. It owes its name from its formation by oxidation of oil of turpentine.

Terephthalic acid is a white crystalline powder, which sublimes without melting; its *dimethyl* ester melts at 140°. The acid is very sparingly soluble in water, alcohol, acetic acid, ether, or chloroform. When heated with lime it yields benzene. Phthalic acid precipitates terephthalic acid from its salts in solution.

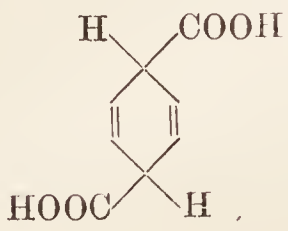
Terephthalic acid in the form of its chloride has been condensed with α-amino-anthraquinone in nitrobenzene solution, and is said to produce a yellow dye (D. R. P. 216980; Eng. Pat. 27098; Frdl. 1908–1910, 753).

For other derivatives, *see* Wegscheider and Faltis (Monatsh. 1912, 93, 141); Kauffmann and Weissel (Annalen, 1912, 393, 1); Hantzsch, Clark and Andrich (Ber. 1915, 48, 785); Lyons and Reid (J. Amer. Chem. Soc. 1917, 39, 1727); Cohen and De Pennington (Chem. Soc. Trans. 1918, 57).

Hydro-terephthalic Acids.

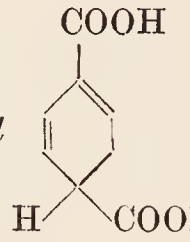
By reducing terephthalic acid with sodium amalgam in aqueous solution through which a stream of carbon dioxide was passed, Baeyer (Annalen, 1888, 245, 142; 1889, 251, 257; 1892, 269, 148) was able to show that two atoms of hydrogen attach themselves to the α-carbon atoms in the molecule.

Trans-$\Delta^{2,5}$-*dihydroterephthalic acid*

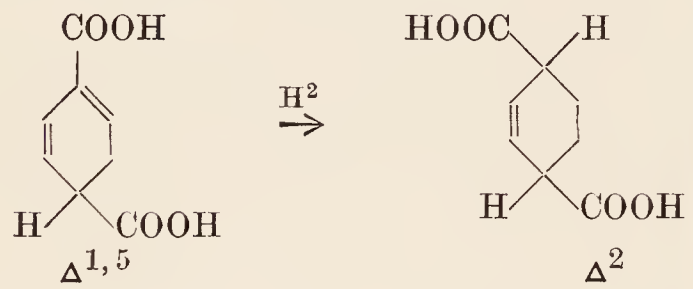


crystallises out first from the acidified product, and may be characterised by its methyl ester, m.p. 77°; the acid seems to have no definite melting-point.

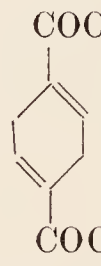
The *cis*-$\Delta^{2,5}$-acid is extracted from the mother liquors by means of ether; its salts are more soluble than those of the *trans*-form. The *trans*-form may also be prepared by electrolysis of a warm alcoholic solution of terephthalic acid containing aqueous sulphuric acid (Mettler, Ber. 1906, 39, 2933). Alkaline permanganate reconverts it into terephthalic acid. As the double linkings are both situated in $\beta\gamma$ positions, inversion into acids containing $\alpha\beta$- double linkings is readily effected. This takes place in two stages, giving the $\Delta^{1,5}$- and $\Delta^{1,4}$-acids—

$\Delta^{1,5}$-*Dihydroterephthalic acid*  is

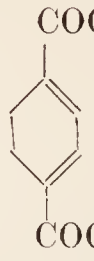
obtained by boiling the above $\Delta^{2,5}$-acid with water, and may therefore be prepared directly from terephthalic acid by reduction in hot solution. Its *methyl ester* melts at 40°. Further treatment with sodium amalgam produces the Δ^{2}-*tetrahydro* acid, following the rule that it is only $\alpha\beta$ double-bonds which undergo reduction under these conditions—



$\Delta^{1,5}$ Δ^{2}

$\Delta^{1,4}$-*Dihydroterephthalic acid*  is

obtained from either the $\Delta^{2,5}$- or $\Delta^{1,5}$-acid by warming with caustic soda, both double bonds being now in $\alpha\beta$ positions. It is therefore readily prepared by reducing terephthalic acid with sodium amalgam in alkaline solution. The *methyl ester* melts at 130°.

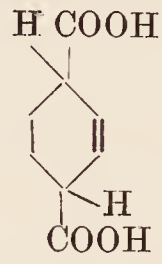
$\Delta^{1,3}$-*Dihydroterephthalic acid*  is

prepared indirectly from the dibromide of Δ^{2}-tetrahydroterephthalic acid by the action of methyl alcoholic potash. Its *methyl ester* melts at 85°. In accordance with Thiele's view of the reduction of conjugated double linkings, it reduces to Δ^{2}-tetrahydroterephthalic acid.

Δ^{1}-*Tetrahydroterephthalic acid*  is

prepared by boiling 1 part of terephthalic acid in caustic soda for 40 hours, and gradually adding 100 parts of sodium amalgam (4 p.c.). It melts above 300°; the *methyl ester* melts at 39° (Baeyer, Ber. 1886, 19, 1805; Annalen 1888, 245, 160; 1890, 258, 32).

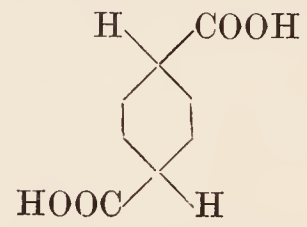
Trans-Δ^{2}-*tetrahydroterephthalic acid*



melts about 220°, and is obtained from the $\Delta^{1,5}$-dihydro acid or from the dibromo-$\Delta^{1,3}$-acid by reduction. The *methyl ester* melts at 3°.

Cis-Δ^{2}-*tetrahydroterephthalic acid* is formed together with the *trans*-form by reducing the $\Delta^{1,4}$-dihydro-acid with sodium amalgam in the cold.

Trans-hexahydroterephthalic acid



is formed on heating the tetrahydro acids with aqueous hydriodic acid at 240°. It melts at 300°; its *methyl ester* melts at 71° (Baeyer, Ber. 1886, 19, 1806; Annalen, 1888, 245, 170; 1889, 251, 257). Its synthesis has been accomplished by Mackenzie and Perkin (Chem. Soc. Trans. 1892, 61, 174).

The *cis*- form, m.p. 162°, is obtained by reducing the very soluble bromo-hexahydroterephthalic acid with zinc dust and acetic acid. Its methyl ester does not crystallise.

2 : 5-**Dichloroterephthalic acid** has been prepared by Bocchi (Gazz. chim. ital. 26, ii. 406) from the dichlorocymene by oxidation with nitric acid.

Terephthalaldehyde is prepared exactly as described in the case of phthalaldehyde (Annalen, 1906, 347, 110). It forms long needles, m.p. 116° (Wegscheider and Suida, Monatsh. 1912, 33, 999).

Terephthalaldehyde acid $COH{\cdot}C_6H_4{\cdot}CO_2H$, colourless rhombic prisms, m.p. 256°. The *methyl ester* forms colourless needles, m.p. 62°–63°, b.p. 265°. The *ethyl ester* is a liquid. The *chloride* colourless prisms, m.p. 45°, b.p. 258°. For other derivatives, *see* Simonis, Boehme and Benenson (Ber. 1912, 45, 1584); Wegscheider and Suida (Monatsh. 1912, 33, 999); D. R. P. 243749.

PHTHALIC ANHYDRIDE *v.* PHTHALIC ACID.

PHTHALIDE *v.* LACTONES.

PHTHALIMIDE *v.* PHTHALIC ACID.

PHYCITE. Identical with erythrol (*q.v.*).

PHYLLITE *v.* SLATE.

PHYSOSTIGMINE, PHYSOSTEGMOL, PHYSOVENINE *v.* ORDEAL BEAN.

PHYTIN, calcium magnesium inositol hexaphosphate

$$C_{12}H_{22}O_{44}P_{10}Ca_7Mg$$

occurs in many plant seeds. In cotton-seed meal, oats, maize, mustard seed, bran, in the seeds of red-fir, peas, beans, pumpkin, red and yellow lupin, and in the potato and other tubers and bulbs, the greater part of the phosphorus exists in this form (Patten and Hart, Amer. Chem. J. 1904, 31, 564).

It occurs to the extent of 2 p.c. in wheat bran and 8 p.c. in rice bran (Suzuki and others, Bull. Coll. Agric. Tokyo, 1907, 7, 495), and is prepared from the latter by extraction with 0·2 p.c. hydrochloric acid. It is purified by precipitating with magnesia, washing the preparation, dissolving in acid and decolorising with charcoal, and again precipitating with magnesia (Contardi, Atti R. Accad. Lincei. 1909, [v.] 18, i. 64). It is a snow-white amorphous powder. It is soluble in water and dilute alcohol; insoluble in benzene, ether, &c. (Posternak, Compt. rend. 1903, 137, 337, 439). In plants it is associated with an enzyme, *phytase*, by which it is hydrolysed into inositol and phosphoric acid; this hydrolysis can also be brought about by dilute acids or by 20 p.c. caustic soda at 220° (Winterstein, Zeitsch. physiol. Chem. 1908, 58, 118; *see* also Neuberg, Biochem. Zeitsch. 1908, 9, 557; Levene, *ibid.* 1909, 16, 399; Neuberg, *ibid.* 1909, 16, 406; 1914, 61, 187; Jegorov, *ibid.* 1912, 42, 432; 1914, 61, 41; Egorov, Bied. Zentr. 1912, 42, 66).

The solution of the pure acid is stable and, when administered to animals by the mouth, has no ill effects (Mendel and Underhill, Amer. J. Physiol. 1906, 17, 75); 35 p.c. is absorbed by the organism, the remainder being eliminated as inorganic phosphates (Horner, Biochem. Zeit. 2, 428; *cf.* Anderson, J. Biol. Chem. 1912, 12, 97; 1914, 17, 171; 1915, 20, 475; Boutwell, J. Amer. Chem. Soc. 1917, 39, 491; Plimmer and Page, Biochem. J. 1913, 7, 157). According to Clarke (Chem. Soc. Trans. 1914, 535) phytin is a complex calcium magnesium salt of an inositol-phosphoric acid and phosphoric acid, and on removing the bases yields the two acids. Inositol phosphoric acid or *phytic* acid has been variously regarded as $C_6H_{18}O_{24}P_6$ (Posternak), or as an inosital ester of pyrophosphoric acid, of the formula $C_6H_{12}O_{16}P_4$ (Anderson).

PHYTOL $C_{20}H_{40}O$, an open-chain primary alcohol containing an ethylenic linkage, derived from chlorophyll by the action of *chlorophyllase*, *v.* Willstätter, Schuppli and Mayer (Annalen, 1919, 418, 121).

PHYTOSTEROL (phytosterin)

$$C_{26}H_{44}O,H_2O, \text{ or } C_{27}H_{46}O$$

s vegetable cholesterol (Hesse, Annalen, 1872, 192, 175). It is contained in calabar beans, in the bark of *Hamamelis virginiana* (Linn.) (Grüttner, Arch. Pharm. 1898, 236, 278); in the bark of *Berberis*; in *Ergot*, in the leaves of *Eriodictyon crassifolium* (Benth.) (Power and Tutin, Pharm. Rev. 1906, 24, 300); in prunas bark (Finnemore, Pharm. J. 1910, [iv.] 31, 604); in the dried rhizome and roots of the yellow jasmine (Moore, Chem. Soc. Trans. 1910, 2226), and of the *Cimcifuga racemosa* (Nutt.) (Finnemore, Pharm. J. 1910, [iv.] 31, 142); in the lichen, *Endocarpon miniatum* (L.) Ach. (Hesse, J. pr. Chem. 1898, [ii.] 58, 465); in the resins of india-rubber, in wheat germs, in the wild cherry bark, in rape oil, in cocoanut, cotton-seed, and in nearly all vegetable oils, and in various lamp oils (Marcusson, J. Soc. Chem. Ind. 1901, 484). It has also been found, probably in the form of esters, in certain peaty soils (Schreiner and Shorez, Chem. News, 1912, 105, 40). *See* also Kerstein (Chem. Zentr. 1899, ii. 91); Mügge (Zeitschr. Nahr. Genuss. 1898, 1, 45); Schmidt and Kerstein (Arch. Pharm. [iii.] 28, 49); Matthes and Rohdich (Ber. 1908, 41, 19, 1591); Matthes and Ackermann (*ibid.* 2000); Cohen (Arch. Pharm. 1908, 246, 515, 592); Power and Rogerson (Pharm. J. 1909, [iv.] 29, 7; *ibid.* 1910, [iv.] 30, 326); Sani (Chem. Zentr. 1903, i. 93); Tarbouriech and Hardy (*ibid.* 1907, ii. 969); Sanders (Arch. Pharm. 1908, 246, 165); Matthes and Heintz (*ibid.* 1909, 247, 161); Klobb (Compt. rend. 1909, 149, 999); Power and Moore (Chem. Soc. Trans. 1909, 246, 1987); Dorée (*ibid.* 649); Rogerson (*ibid.* 1910, 1012); Menozzi and Moreschi (Chem. Zentr. 1910, i. 1777); Matthes and Boltze (Arch. Pharm. 1912, 250, 211); Matthes and Streicher (*ibid.* 1913, 251, 438); Henry (Chem. Soc. Trans. 1920, 1624).

Extraction.—The seeds, bark, or leaves are treated with ligroin, the solution is then evaporated, the residue dried between filter paper and crystallised from alcohol. From oils and fats phytosterol is obtained by saponification with alcoholic alkali and subsequent extraction with ether (Raumer, Zeitsch. angew. Chem. 1898, 24, 555; Wolf, Chem. Zeit. 1898, 22, 805; Heiduschka and Gloth, Pharm. Zentr.-h. 1909, 50, 333). Phytosterol crystallises in needles and in plates, is soluble in chloroform, but insoluble in water and in alkalis, and gives the same reaction as cholesterol with chloroform and sulphuric acid. It has m.p. 132°–136°, but this, as well as its constitution, varies with the source from which it is obtained.

Windaus and Hauth have resolved the crude phytosterol of calabar beans into two constituents: (1) *stigmasterol* or *β-phytosterol*, $C_{30}H_{50}O,H_2O$ or $C_{32}H_{48}O,H_2O$, m.p. 170°; $[\alpha]_D$–45·01° at 21° in $CHCl_3$, which gives a sparingly soluble *bromide* and an *acetate*, m.p. 141°, and a *tetra-bromo-acetate* decomposing at 211°–212°.

(2) *Sitosterol* or *α-phytosterol*, $C_{27}H_{46}O$ or $C_{27}H_{44}O$, m.p. 136°–137° $[\alpha]_D$–34·4° in chloroform, which is identical with the phytosterol contained in wheat germs (Burian, Monatsh. 1897, 18, 551). It yields a readily soluble bromide, and when reduced with sodium and alcohol forms *dihydrophytosterol*, $C_{27}H_{48}O$, m.p. 175°, the dichloride of which on reduction yields *dihydrophytostene*, $C_{27}H_{48}$, m.p. 80°–81°. It is probable that most of the phytosterols of m.p. about 135° consist entirely or chiefly of sitosterol (Ber. 1906, 39, 4378; *ibid.* 1907, 40, 3681; Pickard and Yates, Chem. Soc. Trans. 1908, 1929; Windaus and Welsch, Ber. 1909, 42, 612). According to Thoms (Arch. Pharm. 1897, 235, 39), the term phytosterol should be given to all

unsaturated alcohols of high molecular weight, which give the characteristic cholesterol colour reactions and which owe their origin to physiological processes similar to those producing cholesterol.

Phytosterol gluosides (*phytosterolins*) occur in plants, either as sitosterol *d*-glucosides

$$C_{27}H_{45}O\cdot C_6H_{11}O_5$$

or as the gluosides of stigmasterol

$$C_{30}H_{49}O\cdot C_6H_{11}O_5$$

The sitosterol-*d*-gluoside has been synthesised by Salway by treatment with bromoacetoglucose in ethereal solution in presence of dry silver oxide (Chem. Soc. Trans. 1913, 1022; *cf.* Power and Salway, *ibid.* 1913, 399, 406).

Phytosterol esters may be obtained by heating the alcohol with 5 times its weight of the required acid or anhydride in a sealed tube on the water bath. The melting-points of some of the esters differ with the source of the phytosterol, but in all cases they are considerably higher than the corresponding cholesterol esters, and this can be used as one method of distinguishing between the two alcohols (Bömer and Winter, Zeitsch. Nahr. Genussm. 1901, 4, 865; Jaeger, Rec. trav. chim. 1907, 26, 311; Menozzi and Moreschi, *l.c.*); for other methods compare Kreis (Chem. Zeit. 1899, 23, 21); Ottolenghi (Atti R. Accad. Lincei, 1906, [v.] 15, i. 44); Jaeger (Rec. trav. chim. 1906, 25, 334). The separation of phytosterol from cholesterol is based on the difference of the solubility of their dibromides in a mixture of ether and glacial acetic acid (Windaus, Chem. Zeit. 1906, 30, 1011). The phytosterol in the acetone extract or rubber may be determined by boiling the residue left after the evaporation of the acetone with acetic anhydride under a reflux condenser for 3 hours, whereby the phytosterol, lupeol, and α- and β-amyrols are converted into their respective acetates. The acetic anhydride solution of the acetates is diluted with water and boiled for 3 hours under a reflux condenser to convert the acetic anhydride into acetic acid. The crystalline acetates are separated, washed with hot water, and boiled with standard alcoholic potassium hydroxide solution, the excess of which is titrated. Each gram of potassium hydroxide neutralised by the acetic acid from the acetates corresponds with 7·393 grams of phytosteryl acetate or 6·625 grams of the resin (Dubose, J. Soc. Chem. Ind. 1917, 464). For the detection and estimation of phytosterol in fats, *see* Kreis and Wolf, Chem. Zeit. 1898, 22, 805; Focrster, *ibid.* 1899, 23, 188; Wirthle, *ibid.* 250; Kreis and Rudin, *ibid.* 986; Juckenack and Hilger, Arch. Pharm. 1898, 236, 367; Ritter, Chem. Zeit. 1901, 25, 872; *ibid.* 1902, 26, Rep. 100; Prescher, Zeitsch. Nahr. Genussm. 1917, 33, 77, 481; Klostermann and Opitz, Zeitsch. Nahr. Genussm. 1914, 28, 138; Olig, *ibid.* 1914, 28, 129; Wagner, *ibid.* 1915, 30, 265; Kühn, Bengen and Werwerinke, *ibid.* 1915, 29, 321; Pfeffer, *ibid.* 1916, 31, 38).

For other literature on phytosterol, compare Power and Tutin (Chem. Soc. Trans. 1908, 909); Molinari and Fenaroli (Ber. 1908, 41, 2785); Heiduschka and Gloth (Chem. Zentr. 1908, ii. 1519).

PICAMAR $C_{10}H_{14}O_3$ is easily obtained from wood tar; preferably from birch tar, which contains it in largest quantity. It is isolated by means of its potassium compound, which is purified by recrystallisation and decomposed by an acid; is a colourless, highly-refracting oil; b.p. 290° (corr.); and of sp.gr. 1·10228 at 15°. It has a bitter taste, savouring of peppermint, and a characteristic smoky smell. It is only slightly soluble in water, but freely soluble in alcohol or acetic acid. Its most characteristic reactions are the intense blue-green coloration which it gives with ferric chloride in alcoholic solution, and the insoluble compounds it forms with the alkalis and alkaline earths. Heated with hydrochloric acid at 140° it is decomposed with formation of methyl chloride, and a crystalline product (m.p. 80°) identical in composition and properties with the substance similarly obtained by Hofmann (Ber. 11, 329) from dimethylpropylpyrogallol. This resolution of picamar may be expressed by the equation

$$C_{10}H_{14}O_3+HCl=C_9H_{12}O_3+CH_3Cl$$

The diaceto- derivative $C_{10}H_{12}(C_2H_3O)_2O_3$ is easily obtained by boiling picamar (one part) with acetic anhydride (two parts) for two hours. Recrystallised from alcohol, it is obtained in long colourless needles (m.p. 83°). This is converted by the action of bromine into the dibromo derivative $C_{10}H_{10}Br_2(C_2H_3O)_2O_3$. The potassium compound of picamar $C_{10}H_{12}K_2O_3$ is easily obtained by the addition of alcoholic potash to the alcoholic solution of the substance. The above results indicate that picamar is the monomethyl derivative of a higher homologue of pyrogallol, probably propylpyrogallol, and may be represented therefore by the constitutional formula: $MeO\cdot C_6H_2(C_3H_7)(OH)_2$.

According to Mauthner (J. pr. Chem. 1921, [ii.] 102, 36) picamar may be synthesised by the reduction of 4-acetoxy-3·5-dimethyloxyallylbenzene by hydrogen in presence of colloidal palladium and subsequent hydrolysis of the 4-acetoxy-3·5-dimethoxypropylbenzene. Hence picamar would appear to be 4-hydroxy-3:5-dimethoxy-*n*-propyl-benzene.

PICEA. The spruce-firs: a genus of trees belonging to the conifers, the most important European member of which is the Norway Spruce (*P. excelsa*), constituting the 'White Norway,' Christiania, and Danzig deals of the timber merchant, much used for flooring, joists, and rafters. The waste portions of the trunks and smaller branches are made into splints for the match manufacturer (*v.* MATCHES). Spruce wood is also used in the manufacture of paper (*v.* CELLULOSE). 'Spruce rosin' or 'frankincense' is mainly obtained from *P. excelsa*, and is used in making the better varieties of Burgundy pitch (*v.* BURGUNDY PITCH). The bark and young cones of spruce are employed as tanning materials by the Norse peasantry and an infusion of the buds in milk is used by them as a remedy for scurvy. Spruce beer is made by adding a decoction of the green cone to the wort before fermentation. The needles of the Norway spruce, common silver fir (*Abies alba*), and some other conifers are used in the manufacture of 'pine wool' or 'forest wool,' which is spun and woven with cotton or wool to make 'hygienic flannel.' The black spruce (*P. nigra*) is chiefly found in Canada and Newfoundland. The spruce beer of America is made from the young shoots of this tree: the

concentrated infusion of the buds constitutes 'Essence of Spruce.' Another species found in Canada is the White Spruce (*P. alba*).

Closely allied to *Picea* is *Tsuga*, including the Hemlock Spruce (*T. canadensis*), the bark of which is used for tanning.

Another ally is the Douglas fir (*Pseudotsuga Douglasii* and *P. macrocarpa*), which frequently rises to a height of 200 feet with a trunk measuring 8 to 10 in diameter: its timber is imported as Oregon pine.

PICEIN $C_{14}H_{18}O_7$, a gluoside isolated by Tanret (Compt. rend. 119, 80) from the needle of *Pinus picea*. Silky prismatic needles with a bitter taste, soluble in water and in boiling alcohol, insoluble in ether and chloroform. Lævogyrate $[\alpha]_D = -84°$, m.p. 194°. By hydrolysis yields *piceol* $C_8H_8O_2$, m.p. 109°. Picein has been synthesised by Mauthner (J. pr. Chem. 1913, [ii.] 88, 764) by condensing β-acetobromoglucose with *p*-hydroxyacetophenone and hydrolysis of the resulting tetra-acetogluco-*p*-hydroxyacetophenone.

PICENE. Picene is contained in the least volatile portions of the residues from the rectification of petroleum. It is one of the least soluble constituents, and is best obtained by continual boiling with heavy coal-tar oils and a small quantity of strong sulphuric acid. Picene forms small colourless lamellæ, slightly affected by ordinary solvents, the best being aniline, toluene, and the heavy coal-tar oils. Strong sulphuric acid dissolves it, forming, when pure, a colourless solution exhibiting a pale blue fluorescence. The impure hydrocarbon usually forms an emerald-green solution. It forms conjugated sulpho acids, characterised by the beautiful blue-green fluorescence of their aqueous solutions. Picene melts at 335° to 337°, and boils at 518° to 520°. Its vapour density is 9·77, the formula $C_{22}H_{14}$ requiring 9·56. With picric acid it forms a red crystalline compound, easily decomposed by water and alcohol. It is an orange-red crystalline powder, which, on heating, is partly decomposed and partly volatilised in the form of thin needles. The latter melt at 190°, are insoluble in water and sodium bisulphite, but easily soluble in cold sulphuric acid. When strongly heated with zinc-dust, picene is obtained, and at a lower temperature picene-oxide, a yellow compound which resembles picene, melts at 290°, and has the formula $C_{22}H_{12}O$. Dibromopicene $C_{22}H_{12}Br_2$ is obtained by brominating a solution of picene in chloroform. It forms long white needles, melting at 294° to 296°. The so-called 'crackene' isolated from the 'red pitch' formed in 'cracking' of oils is identical with picene (Meyer and Lendenfeld, Monatsh. 1916, 37, 681).

PICOLINE, PICOLINIC ACID *v.* Bone oil.

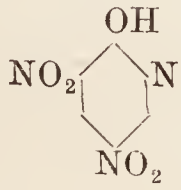
PICOTITE *v.* Spinel.

PICRAMIC ACID *v.* Nitrophenols.

PICRASTOL. Trade name for dimethylodiformylmethenyltetramethylenepentamine.

PICRATOL. Syn. for silver picrate.

PICRIC ACID $C_6H_2(NO_2)_3OH$, or *symmetrical trinitrophenol*,



is the oldest artificial organic dyestuff, having been first prepared by Woulfe in 1771 by the action of strong nitric acid on indigo, who remarked upon its remarkable faculty for dyeing silk a bright yellow shade. Haussmann repeated this preparation in 1788, and investigated its acid properties, observing too its extremely bitter and nauseating taste (J. Phys. March, 1788). Welter obtained it later as a degradation product of silk with nitric acid (Ann. chim. [i.] 29, 301), and Liebig was the first to analyse the substance, describing its salts and giving it the name carbazotic acid (Schweigger's Ann. 47, 373). Its present name of *picric acid* (Greek $\pi\iota\kappa\rho o\varsigma$ = bitter) is due to Dumas, who definitely established its composition. Laurent effected its synthesis from phenol and ascertained its chemical constitution (Ann. chim. [iii.] 3, 221).

Picric acid has been known in the literature under various names, such as yellow gall, bitter yellow, or as chrysolepinic aeid, a name due to Schunck. Concerning picric acid there is an extensive bibliography, much of which is due to early workers at the beginning of last century, when the dyeing properties of this substance were considered important; only a selection of these references can be given here, along with the more recent investigations.

Preparation.—For its laboratory preparation, one part of pure phenol is dissolved in an equal weight of concentrated sulphuric acid, and this solution added to 3 parts of nitric acid of sp.gr. 1·4 in small quantities at a time; after the first energetic action has subsided, the mixture is carefully heated on a water bath for 2 hours. On cooling, the product solidifies to a mass of crystals, which are collected, washed, and recrystallised from hot water (Laurent, Ann. Chim. [iii.] 3, 221).

It has been obtained by the action of hot nitric acid on *indigo* (Woulfe); *aloes* (Schunck, Annalen, 39, 7; 65, 234; *cf.* Marchand, J. pr. Chem. [i.] 44, 91); *Botany Bay* or *Acaroid resin*, the resin of *Xanthorrhœa hastilis* (R. Br.) (Stenhouse, Chem. Soc. Mem. 3, 10; Bolley, W. J., 1858, 460; Wittstein, Dingl. J. 216, 272); *gum benzoin* (Lea, Sillman's Amer. J. [ii.] 26, 381; Kopp, Ann. Chim. [iii.] 13, 233); *salicin* (Piria, Annalen, 56, 63); *saligenin*, *salicylic acid*, *phlorizin*, *coumarin*, *balsam of Peru*, *tribromophenol*, the *nitrophenols*, and in general is the ultimate product of the action of nitric acid upon most monophenolic substances (*cf.* Harding, Chem. Soc Trans. 1911, 99, 1585).

Other interesting methods of formation are the following: oxidation of symmetrical trinitrobenzene with potassium ferricyanide; the acidic nature of the nitro groups facilitates the substitution of ·OH for H (Hepp, Ber. 1880, 13, 2346); aqueous sodium carbonate on picryl chloride (Ber. 1870, 3, 98; J. pr. Chem. [ii.] 1, 145).

Manufacture. Picric acid was formerly, and still is, manufactured from acaroid resin (Miller and Irlam, Eng. Pat. 104352, 1916) until Laurent's discovery of the fact that it forms the end product of the nitration of phenol led to the adoption of this method for its production. At first impure phenol, b.p. 160°–190°, was employed (Balard, Wagner's J. 1862, 585), but this was soon replaced by the pure crystallised substance which is now very largely

used. To avoid the violent reaction which ensues on nitrating phenol, and to lessen the amount of resinous by-products, it is usual to sulphonate the phenol in the first instance, and then act on the resulting phenolsulphonic acid with nitric acid (*cf.* Marqueyrol and Loriette, Bull. Soc. chim. 1919, [iv.] 25, 370 ; Marqueyrol, Carré and Loriette, *ibid.* 1920, [iv.] 27, 143 ; King, Chem. Soc. Trans. 1921, 119, 2105). According to Marzell (Chem. News, 37, 145), equal weights of pure crystallised phenol and sulphuric acid (sp.gr. 1·843) are heated by steam at 100° in large iron vessels provided with mechanical stirrers, and the action is allowed to continue until a test specimen is completely soluble in water ; strong nitric acid (4–5 mol. prop. to 1 mol. phenol) is then gradually added to the cooled product, which is kept well stirred until the reaction is complete. In some works the nitration is conducted in a second vessel, the phenolsulphonic acid being first diluted with twice the quantity of water, and then added gradually to the strong nitric acid contained in a stoneware vessel. In either case the picric acid is obtained as an oily, syrup-like mass, yielding large crystals on cooling ; these are broken up, separated from the mother-liquor either in a filter press or centrifugal machine, washed once or twice with cold water, and then recrystallised from water containing about 1 p.c. of nitric acid, or $\frac{1}{10}$ p.c. of sulphuric acid. In this way much of the accompanying resinous matter is removed and the acid is further purified by conversion into sodium salt, insufficient soda-lye or sodium carbonate solution (Lea, Silliman's Amer. J. [ii.] 32, 182) being added in the first instance in order to bring about the separation of the remainder of the resinous matter. The filtered liquor is then rendered distinctly alkaline, whereby practically the whole of the sodium picrate is precipitated, owing to its insolubility in the alkaline liquid, and the precipitate is pressed, washed with cold water, and finally decomposed by adding an excess of sulphuric acid to its solution in boiling water—an excess of acid being employed inasmuch as picric acid is practically insoluble in a solution of sodium bisulphate.

According to King (*l.c.*) the sulphonation mixture consists almost entirely of phenol-4-sulphonic acid, phenol-2 : 4-disulphonic acid, and an excess of concentrated sulphuric acid. When nitric acid acts on the phenol-sulphonic acids in presence of excess of concentrated sulphuric acid, the nitro group replaces the hydrogen of the nucleus ; if the sulphuric acid is dilute, the sulpho groups are replaced by the nitro group, oxalic acid being produced in proportion to the dilution of the acid.

An increased yield of picric acid is said to be obtained by heating phenol with pyrosulphuric acid at 100°–110°, and nitrating the resulting phenoltrisulphonic acid at 100° by the gradual addition of the calculated quantity of sodium nitrate (Eisenmann and Arche, D. R. P. 51321 of May 8, 1889 ; Eng. Pat. 4539 of 1889).

E. de Lom de Berg has patented a method for the preparation of picric acid from crude phenol (D. R. P. 51603 of June 9, 1889 ; Eng. Pat. 18904 of 1889). The crude material is either fractionally sulphonated—the first fractions consisting of phenolsulphonic acid, which is subsequently nitrated—or converted wholly into sulphonic acid, and the mixture of sulphonic acids fractionally nitrated, the last fractions consisting of picric acid. The sulpho derivatives of the cresols are very soluble in water.

Köhler (D. R. P. 67074 ; Frdl. 1890–1894, 804) describes a process consisting in heating 100 parts phenol with 1000 parts concentrated sulphuric acid for 2 hours at 170°, which gives rise to phenol disulphonic acid ; 96 parts (1 molecule) of dry powdered Chile saltpetre are now added and heated to 140°. This nitrophenol-disulphonic acid is diluted with 320 parts of water and heated to 80°–90° with 244 parts Chile saltpetre, allowing the temperature to reach 140° in about 2 hours.

Gutensohn (D. R. P. 126197 ; Frdl. 1900–1902, 116) proposes to obviate the explosive violence of the direct nitration of phenol by adding a solution of phenol in heated paraffin oil, or other similar mineral oil, to strong nitric acid which has also been covered by a layer of paraffin, further quantities of this oil being added from time to time to dissolve all the phenol.

Wichardt (Fr. Pat. 345441 of 1904 ; Frdl. 1905–1907, 131) suggests a method of preparing picric acid without external heating, by admixture with aliphatic alcohols. A 95 p.c. yield is obtained when 20 parts phenol are mixed, by constant stirring, with 100 parts nitric acid (sp.gr. 1·4) and 30 parts alcohol. Crude picric acid separates on cooling.

Wenghöffer (D. R. P. 125096 ; Eng. Pat. 16371 of 1900 ; Frdl. 1900–1902, 115) has used aniline as the initial material, converting this into sulphanilic acid, and treating the diazotised product with nitric acid ; 50 grams aniline yield 110 grams picric acid.

In the process of Wolffenstein and Böters (D. R. P. 194883 ; Eng. Pat. 17521 of 1907 ; Frdl. 1908–1910, 141, 142) 400 grams benzene, 1350 grams nitric acid (sp.gr. 1·39), and 50 grams mercuric nitrate are mixed and warmed on the water-bath. The products are 380 grams picric acid, 160 grams nitrobenzene, 2 grams *o*-nitrophenol. The nitrobenzene is removed by distillation, leaving crude picric acid as the residue. Oxides of nitrogen may be substituted for nitric acid in presence of either mercury or its salts (D. R. P. 214045). Fuller details of the more modern methods of working are given in Escale's Nitrosprengstoffe, 1915, 177 ; and in Colver's High Explosives, 1918, 295.

Picric acid is now made from dinitrophenol obtained by hydrolysis of chlorodinitrobenzene (*q.v.*)

The Government regulations for the manufacture of picric acid regard it as an explosive except when it contains not less than half its weight of moisture.

Properties. Picric acid crystallises from water or alcohol in lustrous, bright yellow leaflets, and from ether in rhombic prisms melting at 122·5° ; it sublimes when cautiously heated, but explodes if heated rapidly (Berthelot, Ann. Chim. [iv.] 16, 21). When pure it is only very slightly hygroscopic.

It is sparingly soluble in cold, but more readily soluble in hot, water, 1 part of the acid dissolving in 166 parts of water at 5°, in 86 parts at 15°, 81 parts at 20°, 77 parts at 22·5°, 73

parts at 26°, and in 26 parts at 79° (Marchand, J. pr. Chem. [i.] 44, 92).

Dolinski (Ber. 1905, 38, 1836) gives the following data as to the number of parts of water required to dissolve it at various temperatures—

Temp. . .	0°	20°	40°	60°	80°	100°
Parts of water	147·0	90·0	56·2	35·0	22·6	13·8

The solution is more intensely coloured than the ordinary crystallised salt, and dyes the skin and animal fibres a deep yellow; 1 m.g. of acid in a litre of water colours the solution quite appreciably.

Picric acid dissolves readily at ordinary temperatures in alcohol or moist ether, and in about 10 parts of benzene; it is also soluble in concentrated sulphuric acid, forming a colourless solution, from which the picric acid may be partially precipitated on dilution. Its alcoholic solution is antiseptic, and may be used for treating minor cuts and punctured wounds, &c.

Picric acid can be obtained in *colourless* crystals on recrystallising from concentrated hydrochloric acid (W. Marckwald, Ber. 1900, 33, 1128). By washing these crystals with water they develop a yellow colour, and the almost colourless mother liquor also becomes yellower on dilution with water. If ordinary picric acid be dried over concentrated sulphuric acid in a vacuum desiccator, it gradually assumes a lighter colour, and ultimately becomes almost colourless. Pure and perfectly dry picric acid may therefore be considered a colourless compound.

It has been proposed to explain these facts by the dissociation theory; as with other strong acids, ionisation is effected in presence of a mere trace of water, forming $C_6H_2(\overline{N}\dot{O}_3)_3O$— and $\overset{+}{H}$, the former complex ion being yellow. If, however, to this ionised solid or to its aqueous solution another strong acid like hydrochloric or sulphuric acid is added, then the picric ions associate again, the complex ions disappear as such, and the solution becomes paler. Ordinary or moist picric acid and the fused acid are both yellow; even specimens of the almost colourless acid give an intensely yellow melt. A striking illustration of these facts may be obtained by shaking commercial picric acid with light petroleum; as the solvent is a non-dissociating medium a colourless solution is obtained, containing, however, only little picric acid. If the colourless petroleum solution be now shaken with water, the solution becomes intensely yellow. Nearly colourless picric acid separates from hot concentrated solutions of light petroleum as white crystals on cooling. Similar bleaching effects on desiccation have been observed on fabrics themselves dyed with picric acid by Dreaper and Stokes (J. Soc. Dyers, Col. 1909, 25, 10; *cf.* Dehn and Ball, J. Amer. Chem. Soc. 1917, 39, 1381).

Anhydrous ethyl ether dissolves picric acid only sparingly, and the solution is colourless until a trace of water be admitted, when the colour develops, and much more picric acid can now be developed in the moist ether (Bougault, J. Pharm. Chim. 1903, [iii.] 18, 116).

It has been stated by Vignon (Compt. rend. 1909, 148, 844) that the depth of colour of a picric acid solution varies according to its conductivity. Aqueous solutions dye wool and then become impoverished when their conductivity diminishes to a certain value. This impoverishment can also be brought about by adding hydrochloric acid. The fixation of the dye on the fibre Vignon ascribes to the action of the highly ionised dyestuff, the complex coloured ions combining with the fibre; it would seem, therefore, to be not a salt-forming phenomenon (*cf.* von Georgievics, Ber. 1906, 39, 1536; Sommerhoff, Zeit. Farb. Ind. 1906, 5, 270).

Stepanoff (Annalen, 1910, 373, 219) states that the solubility of picric acid in water decreases by the addition of hydrochloric acid, until it reaches a minimum when the solution contains roughly 0·5 millimolecule of picric acid and 150 millimolecules of the mineral acid in 100 c.c. of solution, after which the solubility increases as the concentration of hydrochloric acid becomes greater. He explains this change as being due to an additive compound of picric acid and hydrochloric acid, which is stable only in definite concentrations of hydrochloric acid, and dissolves readily in this acid when the concentration favourable to the existence of the addition compound is reached (*cf.* also J. Russ. Phys. Chem. Soc. 1910, 42, 495).

Other solubility measurements in various media, and various other physical properties, have been observed by Findlay (Chem. Soc. Trans. 1902, 81, 1219), Sisley (Bull. Soc. chim. 1902, [iii.] 27, 901), Marchand (J. pr. Chem. 1848, [i.] 44, 91), Dolinsky (Ber. 1905, 38, 1835), Drucker (Zeitsch. physikal. Chem. 1903, 46, 827; 1904, 49, 563), Bougault (J. pharm. Chim. 1902, [iv.] 18, 116), Gorke (Zeitsch. physikal. Chem. 1908, 61, 495).

Fused picric acid attacks metals only slightly. According to Saposchnikoff (Zeitsch. ges. Schiess. Sprengstoffen, 1911, i. 852) in proportion to the equivalent amount of the metal. Tin does not appear to be attacked.

Addition-compounds. Picric acid possesses the property of combining in molecular proportions with many aromatic hydrocarbons and phenols, giving crystalline additive compounds with a fair degree of stability (Fritzsche, J. pr. Chem. [i.] 73, 212; Annalen, 109, 247; Berthelot, Bull. Soc. chim. 1867, 7, 30; Reddelien, J. pr. Chem. 1915, [ii.] 91, 213).

Benzene forms such an addition product $C_6H_6,C_6H_2(NO_2)_3OH$, which crystallises in yellow needles, m.p. 85°–90°; it decomposes at the ordinary temperature in a vacuum desiccator, or by solution in water.

Naphthalene forms a molecular compound on fusion with picric acid or on mixing alcoholic solutions of the two components, yielding golden-yellow crystals, m.p. 149·5°; several eutectic mixtures may also be obtained. It is decomposed by large excess of alcohol (Saposchnikoff and Rdultowsky, J. Russ. Phys. Chem. Soc. 1903, 35, 1073).

The *anthracene* derivative is obtained by mixing concentrated alcoholic solutions of the hydrocarbon and acid, when beautiful ruby-red needles separate having the m.p. 138°; it is resolved into its components on dissolving in a large volume of alcohol, water, or ether (*cf.* Behrend, Zeitsch. physikal. Chem. 1894, 15, 183).

Phenanthrene yields a stable picric acid derivative, which may be recrystallised from alcohol and obtained in golden yellow crystals, m.p. 143° (Hayduck, Annalen, 1873, 167, 177). Ammonia liberates the hydrocarbon in the pure state, affording a means of separation of phenanthrene from anthracene.

Phenol and picric acid form an additive compound which melts at 53°; it decomposes at 100° or in a desiccator over sulphuric acid at ordinary temperatures (Goedike, Ber. 1893, 26, 3042). The same author has made a picrate of *acetophenone*, and suggests the rule that substituted phenols, &c., only form picrates when the substituent is in the *ortho*-position.

α-Naphthol picrate

$$C_{10}H_7(OH),C_6H_2(NO_2)_3OH$$

crystallises in orange-yellow needles, m.p. 189°, and is very soluble in alcohol or ether.

The *β-naphthol* derivative exists as yellow needles, m.p. 155°, readily soluble in alcohol, ether, or chloroform, although decomposed by ammonia. Combination is said to take place according to the law of adsorption, as the amount of compound formed depends on the concentration of the hydrogen ions (Pelet-Jolivet and Henny, Bull. Soc. Chim. 1909, [iv.] 5, 623; *cf.* also Kuriloff, Zeitsch. physikal. Chem. 1897, 23, 90, 673: 24, 441; and Bruni, Gazz. chim. ital. 1898, 28, ii. 508).

For additive products of derivatives of picric acid with nitrogenous aromatic compounds, *see* Ciusa and Vecchiotti, Atti R. Accad. Lincei, 1911 [v.] 20, ii. 377; Sudborough and Beard, Chem. Soc. Trans. 1910, 97, 773; Giua and Marcellino, Gazz. chim. ital. 1920, 50, i. 341.

It has been shown by Bruni and Tornani (Chem. Zentr. 1904, ii. 954) that compounds possessing an allyl grouping, $\cdot CH_2 \cdot CH : CH_2$ in the side chain, like safrol, methyl eugenol, and apiol, do not combine with picric acid, whilst compounds containing the propenyl grouping $-CH=CH \cdot CH_3$ react readily. Dioxymethylene compounds like piperonal, and ketones such as cyclohexanone also form well-defined picrates. Gibson describes the picrate of nitroaniline (Chem. Soc. Trans. 1908, 93, 2100), and Tilden and Forster have prepared a crystalline derivative of *pinene* and picric acid, m.p. 133° (Chem. Soc. Trans. 1893, 63, 1388).

In addition to the above additive products, picric acid forms very characteristic crystalline derivatives with most organic bases like pyridine and the alkaloids, and therefore provides a ready and valuable means for their purification and identification.

Reactions. Phosphorus pentachloride converts picric acid into trinitrochloro-benzene, or picryl chloride, m.p. 83°. Ferrous salts or alcoholic ammonium sulphide reduce the acid to dinitro-aminophenol, or picramic acid, m.p. 168°–169°, which was formerly used as a brown dye (Girard, Compt. rend. 36, 421); whilst aqueous ammonium sulphide reduces it to diaminonitrophenol (Gricss, Annalen, 1869, 154, 202). Complete reduction of all the nitro groups is effected by tin and hydrochloric acid, the triaminophenol thus formed being characterised by the deep blue colour which it gives in aqueous solution with ferric chloride (Roussin, Wagner's J., 1861, 536).

A hot solution of picric acid reacts with potassium cyanide forming a strongly coloured, brown-red solution of picrocyaminic or *iso*-purpuric acid, $C_6H_2(NO_2)_2N(CN)_2OH$, formerly known as the dyestuff, grenat brown (Hlasiwetz, Annalen, 1859, 110, 290; Zulkowsky, Wagner's J., 1868, 661; Kopp, Ber. 1872, 5, 664). A like reaction occurs with the cyanides of all the alkalis and alkaline earth metals, and with magnesium, cadmium and zinc, whilst silver, copper, and mercury cyanides do not show this reaction (Varet, Compt. rend. 112, 339; 119, 562).

Borsche has contributed to our knowledge of this as a general reaction for nitrophenols (Ber. 1900, 33, 2719, 2995; 1903, 36, 4357; 1904, 37, 1843, 4388), and ascribes to *iso*-purpuric acid the constitution

$$C_6(NO_2)_2(CN)_2(OH)NH \cdot OH$$

Boiling picric acid with alkalis seems to eliminate one nitro group as ammonia, and both prussic acid and a nitrate can be detected in the aqueous solution as alkali salts (Wedekind and Haeussermann, Ber. 1902, 35, 1133). Oxidation with hydrogen peroxide in presence of ferrous salts yields an intense green solution, and the product reacts with phenylhydrazine (Fenton and Jones, Chem. Soc. Trans. 1900, 77, 76). Oxidation with chromic acid causes no liberation of nitrogen (Oechsner de Coninck and Combe, Compt. rend. 1899, 128, 239).

Sodium carbonate seems to possess a specific property of precipitating sodium picrate from solution. A single drop of a cold saturated solution of a picrate added to 10 c.c. of a 1 p.c. solution of the carbonate produces a slight turbidity, and with increasing concentration of the carbonate solution, or larger quantities of the picrate, the phenomenon becomes still more conspicuous (Reichard, Zeitsch. anal. Chem. 1904, 43, 269). The potassium salt is very sparingly soluble, and for this reason serves as a qualitative test for potassium.

A *hydrazine picrate* $C_6H_2(NO_2)_3OH,N_2H_4$ is described by Silberrad and Phillips (Chem. Soc. Trans. 1908, 93, 474). Picric acid stains may be removed by a solution of alkaline sulphide or polysulphide, followed by a thorough washing with soap and water (Bougault, J. Pharm. Chim. 1903, 18, 158).

Detection and estimation.—Picric acid is not volatile in steam, and can readily be detected by its bitter taste and the sparing solubility of its potassium salt. The usual tests are five in number, and are given below, with their limits of sensitiveness subjoined: I. The *iso*purpuric acid reaction, showing a blood-red coloration on warming picric acid with potassium cyanide and soda; limit, 1 : 5000. II. The picramic acid reaction, giving rise to a blood-red colour on heating with sodium hydroxide and grape sugar; limit, 1 : 7000. III. Picramic acid reaction with sodium hydroxide and ammonium sulphide; limit, 1 : 12,500. IV. Yellowish-green crystalline precipitate of hexagonal needles, which polarise light, is obtained when ammoniacal solution of copper sulphate is added to picric acid in water; limit, 1 : 80,000. V. By dyeing white wool; degree of delicacy is 1 : 110,000. The reactions II. and V. are less sensitive in presence of fats or other impurities.

Rymsza (Zeitsch. anal. Chem. 1897, 36, 813) describes a method of extracting and treating mixtures containing picric acid only in traces in order that the above tests may subsequently be applicable. The method consists in macerating the substance with dilute sulphuric acid, mixing with 3 volumes of 95 p.c. alcohol and digesting for 24 hours at 50°–60°. After filtration and evaporation of the alcohol, any fat is removed by shaking with light petroleum, and the liquid is then acidified with hydrochloric acid and extracted repeatedly with ether. In cases of picric acid poisoning the urine is always coloured red-brown by presence of picramic acid ; the picric acid may be extracted with ether after simply acidifying, and the above tests, preferably I., applied.

An aqueous solution of picric acid gives with methylene blue in the cold, a violet flocculent precipitate, soluble in ether, chloroform, or hot water. These coloured solutions vary from blue to green. When the solution in chloroform is evaporated, a violet residue is obtained (Swoboda, Chem. Zentr. 1896, ii. 717 ; Zeitsch. anal. Chem. 1897, 36, 513). Lacquers tested in this way for picric acid should first be dissolved in a little alcohol. It is claimed that the picramic acid test (II. and III.) is sensitive to 1 part per hundred thousand if the reduction is effected with sodium hyposulphite in presence of ammonia (Aloy and Frébault, Bull. Soc. chim. 1905, [iii.] 33, 495). Kast (Untersuchung d. Spreng. u. Fundstoffe, Brunswick, 1909, 973) describes acridine chlorhydrate as a test substance for picric acid, 1 part of picric acid in 50,000 parts of solution being recognisable.

Picric acid differs from the nitrocresols in the colorations of its reduction products with stannous chloride and hydrochloric acid.

Rupeau describes the application of the *iso*-purpuric acid test (I.) for the colorimetric estimation of picric acid in beer ; it is claimed that 0·01 gram of acid per litre may thus be recognised (Chem. Zentr. 1897, ii. 813). A reagent is suggested consisting of 5 grams ferrous sulphate, 5 grams tartaric acid, and 200 c.c. of a brine solution ; 0·5 gram of the sample of beer is allowed to flow on to 1–2 c.c. of the above reagent, and 2 drops of ammonia are added, and the mixture gently shaken. A reddish coloration appears, sensitive to 0·005 gram picric acid per litre.

Schwarz (Monatsh. 1898, 14, 139) has used a volumetric method for the determination of nitro derivatives generally, depending upon the liberation of iodine by heating in a closed vessel at 100° with an iodate and iodide. This has been improved by Feder (Chem. Soc. Abstr. 1906, ii. 809), who merely mixes potassium iodide and iodate with the picric acid solution, iodine being liberated, which is estimated by titrating with thiosulphate, using starch solution as indicator. For the evaluation of picric acid salts it is necessary to acidify with mineral acid, extract with benzene, evaporate, and redissolve the residue in water before proceeding with the above titration. The use of a potassium iodide solution after bromination with bromine water, in order to determine the amount of halogen absorbed, is recommended by Allen (Chem. Soc. Trans. 1888, 53, 592). Sinnatt has employed Knecht's method of titration with titanous chloride for the estimation of the additive compound with naphthalene (Chem. Soc. Proc. 1905, 18, 297 ; *cf.* Colman and Smith, Chem. Soc. Trans. 1900, 77, 128). Picric acid in its compounds with organic bases has been estimated colorimetrically by Kutusow (Zeitsch. physiol. Chem. 1894, 20, 166) ; *e.g.* ptomaines are readily separated from mixtures by the addition of picric acid and the compound can be weighed ; but the author recommends the determination of the combined picric acid colorimetrically either by the spectrophotometer, or, better, by the use of Hoppe-Seyler's double pipette (*cf.* Zeitsch. physiol. Chem. 16, 505).

A gravimetric determination of picric acid is given by Busch and Blume (Zeitsch. angew. Chem. 1908, 21, 354), depending upon the precipitation of nitron-picrate, and involving the use of the reagent 'nitron' (described in Ber. 1905, 38, 856). Nitron picrate, which is very sparingly soluble, consists of lemon-yellow needles, and after drying at 110° is weighed ; the weight multiplied by $\frac{229}{541}$ gives the amount of picric acid present in the solution examined. The method is not applicable in presence of hydrobromic, hydriodic, chloric, perchloric nitrous, nitric, or chromic acids.

An alternative method of evaluation, due to Utz (Zeitsch. anal. Chem. 1908, 47, 140), is recorded, in which picric acid is oxidised with hydrogen peroxide in sodium hydroxide solution, and the nitric acid produced is precipitated as insoluble nitron-nitrate and subsequently weighed : 1 gram=0·037406 gram of nitrogen. *See also* Busch and Schneider (Fert. f. Schiess u. Sprengst. 1906, 232) ; and Cope and Barat (J. Amer. Chem. Soc. 1917, 39, No. 3, 504).

Picric acid may be quantitatively estimated by precipitation with acridine, since acridine picrate is very sparingly soluble in cold water (Anschütz, Ber. 17, 439). This method is liable to error, owing to the instability of the picrate in a hot aqueous solution.

Adulterations. Commercial picric acid sometimes contains impurities, which either are by-products—*e.g.* resin, oxalic acid, &c.—formed in its manufacture and insufficiently removed by washing, or are fraudulent additions. According to Winckler (Wagner's J., 1858, 461), the following impurities may be recognised thus :—(1) Resin : dissolve 1 part of picric acid in 60 parts of boiling water, add $\frac{1}{20000}$ of the weight of sulphuric acid and filter. Any resin will be left behind on the filter paper. (2) Oxalic acid : examine the specimen microscopically, or dissolve 1 part in 100 parts of water, and estimate the amount by precipitating with ammonia and calcium chloride solution. (3) Nitre, or sodium sulphate : treat with alcohol to dissolve the picric acid present, and examine the saline residue by the ordinary method. (4) Sugar : neutralise with potassium carbonate, evaporate to dryness, and extract the sugar by repeated treatment with alcohol ; then examine the alcoholic extract for sugar in the usual way.

Casthélaz (Chem. News, 15, 140) states that common salt and alum are sometimes used as adulterants in addition to the foregoing, and treats the specimen with benzene or ether, which extract the whole of the picric acid, but

do not dissolve the oxalic and various salts which may be present.

Uses in Industry.

Dyeing.—Picric acid has the property of dyeing animal fibres and tissues directly in an acid bath, but is not fixed by cotton or other vegetable fibres, unless previously mordanted with albumen or with a mixture of aluminium and magnesium acetates; hence it is sometimes used as a means of detecting cotton in undyed silk or woollen fabrics. Its tinctorial powers are great, and it produces on silk and wool a clear, bright yellow, which, compared with most other yellows, appears to have a greenish shade; but, owing to the colour being fast neither to light nor washing, picric acid is now but little used as a yellow dye, although it is frequently employed to produce compound colours with such dyes as benzaldehyde-green, methyl-violet, indigo-carmine, &c.

For observations on dyeing with picric acid, *see* Walker and Appleyard (Chem. Soc. Trans. 1896, 69, 1334); von Georgievics (Monatsh. 1911, 32, 319).

Picric acid has been used in the preparation of certain other dyestuffs of the nigrosine and induline class; it is fused with various monamines such as aniline and its hydrochloride, in presence of ammonium vanadate, and the spirit-soluble dye converted into water-soluble dye by sulphonation and formation of the sodium salt; a nigrosine colouring matter results. The indulines involve the use of aromatic diamines in a similar manner, and glycerol is added to the melt (D. R. PP. 84293, 84294; Frdl. 1894–1897, 449, 451; *cf.* also Bacovescu, Chem. Zentr. 1908, i. 2034).

Substantive cotton dyes have been prepared from picric and picraminic acids by heating in aqueous solution with sulphur and alkaline sulphides (D. R. P. 116791; Frdl. 1900–1902, 740).

Tanning.—Its use in the leather industry is mentioned by Watenburger (Leather Manufacture, 1901, 12, 54; J. Soc. Chem. Ind. 1901, 596). After tanning the hides with picric acid solution, they are allowed to drain and then transferred to a 1 p.c. tannin extract for 12 hours; they are afterwards washed, partially dried and fat liquored, and finished in the usual way. The picric acid is fixed in the grain of the material in a permanently insoluble form.

Explosives.—Picric acid is usually said to explode on heating, but Berthelot has pointed out (Compt. rend. 105, 1159) that this is only true when very small quantities at a time are suddenly heated, for when heated in any quantity the acid melts and gives off vapours which burn with a luminous flame without explosion; picric acid, moreover, does not under ordinary conditions explode by percussion. The picrates, on the other hand, are readily exploded by heating or percussion, and have been employed as explosives—lead picrate, for example, being used for filling percussion caps (Prat, J. 1874, 1124). Picrates, however, do not contain sufficient oxygen for their complete combustion, and hence mixtures of potassium or ammonium picrate with either nitre or potassium chlorate have been employed (Wagner's J. 1871, 318)—Brugères' picrate powder, for example, consisting of 54 p.c. ammonium picrate and 46 p.c. potassium nitrate (Compt. rend. 69, 716). The volumes of gas liberated by the explosion of lead, strontium, barium, and potassium picrates respectively, and of mixtures of potassium picrate with 45 p.c. of nitre or 50 p.c. of potassium chlorate, have been measured by Roux and Sarrau (Compt. rend. 77, 478; 79, 757), and the volume and composition of the gas, together with the composition of the residue produced by the explosion of potassium picrate under varying pressures, have been determined by Sarrau and Vieille (Compt. rend. 93, 61).

Mixtures of picric and various oxidising agents have been proposed as explosives. Thus a solution of 58·3 parts of picric acid and 41·7 parts of nitric acid (sp.gr. 1·5) explodes with great violence and without smoke when fired with a detonator (Sprengel, Chem. Soc. Trans. 1873, 800), and mixtures of analogous composition stiffened with asbestos have been patented by Punshon (Eng. Pat. 2242 of 1880, 11432 of 1885), whilst Tschirner has patented an explosive consisting of 1 part picric acid, 1 part coal-tar, and 5 parts potassium chlorate (or potassium permanganate in about the same proportion), which is fired by percussion caps (D. R. P. 15508 of Feb. 6, 1880). These mixtures with oxidising agents have the double effect of decreasing the force of the explosion, and at the same time increasing the sensitiveness of picric acid to detonation. Mélinite, one of the most powerful explosives invented, is said to consist solely of compressed picric acid. According to Turpin (Eng. Pat. 15089 of 1885; D. R. P. 38734 of Jan. 12, 1886; Zeitsch. Chem. Ind. 1, 193), picric acid, when obtained in masses (1) by compresssion, (2) by admixture with gum arabic solution or with a suitable fat or oil, or (3) by admixture with 3–5 p.c. of collodion, can be exploded in closed vessels by 1–3 grams of silver fulminate. The best results and the greatest insensitiveness are attained by fusion of the acid, since a mass of fused picric acid cannot be exploded in the open air by detonation with 3 grams of silver fulminate introduced into the interior, although shells, torpedoes, &c., filled with liquid picric acid (fused at 130°–145°), and cooled slowly, can be exploded by a charge of quick-burning gunpowder or a priming of picric acid powder detonated by 1·5 grams of fulminate, the explosion being one of the most destructive known.

An account of the most important metallic salts with their characteristic properties is given below. Their chief interest lies in their explosive nature (*v.* Explosives).

Salts of Picric Acid.

The metallic salts may be prepared by bringing together picric acid and the carbonate or oxide of the metal, and evaporating the solution until crystals appear on cooling. The references to the literature on this section of the subject are too numerous to be given, and, moreover, the results published by different workers are not always concordant. A *resumé* and bibliography is given in a paper by Silberrad and

Phillips (Chem. Soc. Trans. 1908, 93, 474), who reinvestigated several of the metallic salts.

Aluminium salt $[C_6H_2(NO_2)_3O]_3Al,16H_2O$. Pale yellow needles. Changes to *tetrahydrate* at 80°, which is a pale yellow powder decomposing without explosion on heating.

Ammonium salt exists as a yellow and red variety, both anhydrous. They volatilise without detonation on heating. Soluble in water, sparingly so in alcohol.

Barium salt $[C_6H_2(NO_2)_3O]_2Ba,5H_2O$, also $3H_2O$. Deep yellow prisms, sparingly soluble in cold water. It becomes *anhydrous* on heating at 80°, giving a yellow powder which explodes with violence at 333°.

Cadmium salt $[C_6H_2(NO_2)_3O]_2Cd,7H_2O$. Yellow hexagonal plates; yields the *anhydrous* salt at 80°, which is yellow and explodes violently at 336°. A pentahydrate also exists.

Calcium salt $[C_6H_2(NO_2)_3O]_2Ca,10H_2O$, also 3 and $5H_2O$. Yellow plates; yields *anhydrous* salt at 80°, which is a yellow powder exploding with violence at 323°.

Chromium salt is basic and of complex constitution. Green crystals.

Cobalt salt $[C_6H_2(NO_2)_3O]_2Co,9\frac{1}{2}H_2O$. Brown needles. The *hexahydrate* is better known and exists as brown laminæ. Both these give the dihydrate at 80°, and the *anhydrous* salt at 150°, the latter being a brown powder exploding at 320°.

Copper salt $[C_6H_2(NO_2)_3O]_2Cu,11H_2O$. Green prisms, which yield the *anhydrous* salt at 80°. This latter is a greenish-yellow powder, exploding violently at 282°.

Ferric salt $[C_6H_2(NO_2)_3O]_3Fe,11H_2O$. Reddish-yellow crystals.

Ferrous salt $[C_6H_2(NO_2)_3O]_2Fe,8H_2O$. Obtained from barium salt and ferrous sulphate. Yellow hexagonal prisms. Becomes *anhydrous* in vacuum over sulphuric acid, yielding a dark green powder, which explodes feebly at 315°.

Lithium salt $C_6H_2(NO_2)_3OLi,4H_2O$. Yellow prismatic needles, changing gradually into the dark orange-yellow *monohydrate*. This becomes *anhydrous* at 150°, giving a pale yellow powder, which explodes at 318°.

Lead salt $[C_6H_2(NO_2)_3O]Pb,4H_2O$. Silky yellow needles, yielding monohydrate at 80°, and the anhydrous salt at 150°; the last of these is a yellow powder, which explodes violently at 270° and differs from all the other salts in being extremely sensitive to shock or friction.

Magnesium salt $[C_6H_2(NO_2)_3O]Mg,8H_2O$, also 3 and $5H_2O$. Silky, yellow needles. Forms also a *hexahydrate* and *dihydrate*, all of which become anhydrous at 150°. Explodes feebly at 367°.

Manganese salt $[C_6H_2(NO_2)_3O]Mn,8H_2O$. Yellow prisms. At 80° forms *trihydrate*, and at 150° becomes anhydrous; this last is yellow, and explodes with violence at 235°.

Mercury salt $[C_6H_2(NO_2)_3O]_2Hg,4H_2O$. Difficult to prepare, as it tends to pass into the *basic hexahydrate*, the *anhydrous* salt of which volatilises without explosion on heating.

Nickel salt $(C_6H_2(NO_2)_3O]_2Ni,9\frac{1}{2}H_2O$. Green needles. *Hexahydrate* forms green laminæ. Both yield the dihydrate at 80°, and the anhydrous salt at 150°, the latter being a green powder, which explodes at 335°.

Potassium salt $C_6H_2(NO_2)_3OK$, is anhydrous. It crystallises from aqueous solutions in yellow iridescent prismatic needles, and explodes at 311°. Sparingly soluble in cold water.

Silver salt $C_6H_2(NO_2)_3OAg$. Yellow anhydrous salt, exploding feebly at 336°.

Sodium salt $C_6H_2(NO_2)_3ONa,H_2O$. Minute, yellow needles, yielding *anhydrous* salt at 150°, which is a pale yellow powder, exploding feebly at 310°.

Strontium salt $[C_6H_2(NO_2)_3O]_2Sr,5H_2O$, yellow needles, yields *monohydrate* at 80°, and *anhydrous* salt at 200°. Explodes violently at 340°.

Thallous salt exists in enantistropic yellow and red modifications (*cf.* Cohen, Proc. K. Akad. Wetensch. Amsterdam, 1916, 18, 861).

Zinc salt $[C_6H_2(NO_2)_3O]_2Zn,9H_2O$. Yellow prismatic needles; yields *dihydrate* at 80°, and *anhydrous* salt at 150°, which is a brownish-yellow powder, exploding violently at 350°. The *hexahydrate* has been prepared and also an *octohydrate*.

Cf. paper by Kast (Chem. Soc. Abstr. 1911, 100, 852; Zeitsch. ges. Schiess-sprengstoffwesen, 1911, 6, 7).

A *sodium peroxide derivative* of picric acid $C_6H_2(NO_2)_3O—ONa$ has been patented as a very powerful explosive (D. R. P. 96855; Frdl. 1897–1900, 47). It is prepared by heating 5 grams of sodium peroxide in 200 c.c. of water containing 15·9 grams of picryl chloride for 2–3 hours. The solution becomes deep brown, and deposits red-brown prisms on cooling, which are sparingly soluble.

A picra-borate explosive, described by Billet (J. Soc. Chem. Ind. 1900, 1144), is obtained by heating aqueous solutions of sodium borate and picric acid.

Girard (J. Soc. Chem. Ind. 1900, 1144) gives the following method of preparing picrates for explosives: a mixture of 30 kilos. castor oil and 10 kilos. of powdered picric acid is incorporated with the theoretical quantity of the base in the state of carbonate or oxide; the soluble alkalis are used in solutions of 45°Bé. The oil should be present in not less amount than 5 parts to 10 parts of acid. Metallic oxides may be replaced by oleates, stearates, palmitates, &c., the fatty acids dissolving in the castor oil after reaction. The salts are dissolved out with volatile solvents to avoid the inconvenience attending their recovery from aqueous solution.

Ethers of Picric Acid.

Methyl picrate $C_6H_2(NO_2)_3OCH_3$ (*trinitroanisole*). Yellow monoclinic tables, m.p. 64° (Post and Mehrtens, Ber. 8, 1552; Frdl. 1879, 514). Obtained by nitrating anisole. Decomposed by strong potassium hydroxide giving picric acid, and with ammonia giving trinitraniline (Salkowski, Annalen, 1874, 174, 259).

Ethyl picrate $C_6H_2(NO_2)_3OC_2H_5$. Long, almost colourless needles, m.p. 78·5° (Stenhouse and Müllert, Annalen, 1867, 141, 80; Willgerodt, Ber. 1879, 12, 1277). Obtained from methyl ether on recrystallising from ethyl alcohol (Boos, Amer. Chem. J. 20, 449).

Phenyl picrate $C_6H_2(NO_2)_3OC_6H_5$. Needles, m.p. 153°. Prepared from picryl chloride and potassium phenate in aqueous alcoholic solution (Willgerodt, Ber. 1879, 12, 1278).

Acetyl picrate $C_6H_2(NO_2)_3O{\cdot}OC{\cdot}CH_3$. Deep yellow crystals, m.p. 75°. Decomposes, giving acetic acid, at 120°. Obtained from picric acid and acetic anhydride (Tommasi and David,

Annalen, 168, 167; Heinke, Ber. 1898, 31, 1400; v. Pechmann, Ber. 1900, 33, 629). Very soluble in warm alcohol or ether.

OTHER DERIVATIVES.

Picryl chloride $C_6H_2(NO_2)_3Cl$. Crystallises from ether in amber-yellow tables; from alcohol in almost colourless needles, m.p. 83°. Obtained by the action of phosphorus pentachloride on picric acid, or by nitrating chlorobenzene. Like picric acid itself, it combines with aromatic hydrocarbons, forming additive products (Pisani, Annalen, 1854, 92, 326; Liebermann and Palm, Ber. 1875, 8, 378).

Picryl bromide $C_6H_2(NO_2)_3Br$. Elongated, pale-yellow plates, m.p. 122°–123° (Jackson and Earle, Amer. Chem. J. 1903, 29, 212). Obtained by nitrating bromobenzene.

Picryl sulphide, an explosive melting at 213° and almost immediately resolidifying, changing colour and remelting again at 234°. The cause of the change of melting-point is unknown. It explodes in the neighbourhood of 300° (Roche and Thoman, Compt. rend. 1923, 176).

Picramide $C_6H_2(NO_2)_3NH_2$ (trinitraniline). Prepared by action of ammonia on picryl chloride or on ethyl picrate. Dark yellow, monoclinic tables, m.p. 188° (Hepp, Annalen, 1882, 215, 350; Salkowsky, Annalen, 1873, 165, 187).

Picramic acid (4 : 6-*dinitro*-4-*aminophenol*) $C_6H_2(NO_2)_2(NH_2)OH$. Obtained by reduction of picric acid with ammonium sulphide or other mild reagents. Red crystals, m.p. 169° (Girard, Annalen, 1853, 88, 281; Pugh, *ibid.* 1855, 96, 83; Stuckenberg and Rudolf, J. pr. Chem. [ii.] 48, 425). Used formerly as a brown dye.

*iso***Purpuric acid** (picrocyaminic acid, or *grenat brown*) *v. iso*-PURPURIC ACID.

Dichloropicric acid (3 : 5 dichloro-2 : 4 : 6-trinitrophenol) may be obtained by chlorinating *p*-nitroaniline, dissolved in 3 parts of acetic acid and 6 parts by weight of concentrated hydrochloric acid, cooled in ice, and converting the 2 : 6-dichloro-4-nitroaniline into 3 : 5-dichloro-1-nitrobenzene, and reducing this to the amine by iron-filings and hydrochloric acid, transforming it into 3 : 5-dichlorophenol, and nitrating by fuming nitric acid and acetic acid. Dichloropicric acid crystallises in pale yellow prisms, m.p. 139°–140° (corr.), the sodium salt in quadratic prisms and the potassium salt in slender needles, both lemon-yellow (Willstätter and Schudel, Ber. 1918, 51, 782).

PICRIN *v.* DIGITALIS.

PICROGLYCION *v.* DULCAMARA.

PICROLITE *v.* SERPENTINE.

PICROMERITE or **SCHOENITE**. Hydrated double sulphate of potassium and magnesium $K_2SO_4{\cdot}MgSO_4{,}6H_2O$, containing K_2O 23·4 p.c., and crystallised in the monoclinic system. The name picromerite was given to a white crystalline encrustation formed on the lava erupted from Vesuvius in 1855, from the solution of which good crystals (sp.gr. 2·03) were readily recrystallised. In 1866 it was found as a thin crust on kainite at Leopoldshall near Stassfurt. Beautiful water-clear crystals have since been found at Stassfurt, and larger quantities of the mineral have been found at other places in the Prussian salt-deposits; at Westeregeln it forms a capping, 10 metres in thickness, on the kainite, from which it has probably been derived; at Aschersleben in the kainite region; and at Wilhelmshall it forms the base of a bed of sylvite. It is also known from the salt-deposits at Kalusz in Poland and Hallstatt in Austria. L. J. S.

PICROPODOPHYLLIC ACID and **PICROPODOPHYLLIN** *v. Podophyllum resin*, art. RESINS.

PICRORHIZA. The dried rhizome of *Picrorhiza Kurroa* (Royle).

PICROTIN, PICROTOXIDE *v.* PICROTOXIN.

PICROTOXIN. A poisonous crystalline compound, somewhat allied in its physiological action to strychnine, which occurs in 'Cocculus Indicus,' the small, berry-like fruit of *Anamirta paniculata* (Colebrooks) (Bentl. a. Trim. 14), a climbing shrub of Eastern India and the Malayan islands. The drug does not find much favour in Western medicine, but is employed in India. Here it is better known for its power of stupefying fish and causing them to rise to the surface of the water in a state of intoxication, and as a reputed adulterant of malt liquors. On account of its poisonous properties, it sometimes becomes necessary to search for it in beer.

The small, black, ovoid fruit consists of a rough, tasteless pericarp, enclosing a reniform seed, which has an oily and bitter taste. The pericarp does not contain picrotoxin, but Pelletier and Couerbe isolated from it two crystalline compounds: *menispermine*, a base, which melts at 120° and forms a crystalline sulphate, and *paramenispermine*, a neutral constituent which melts at 250°, together with a brown mass, *hypopicrotoxic acid*, which softens at 100° (Ann. Chim. [ii.] 54, 196). Half the weight of the seed is stearin. The *picrotoxin* exists to the extent of 0·4 to 1·0 p.c. It was discovered in 1812 by Boullay (J. Pharm. Chim. [i.] 4, 5).

To prepare picrotoxin, the method of Barth (J. pr. Chem. [i.] 91, 155; J. 1863, 586) and Barth and Kretschy (Monatsh. 1, 98) is usually followed. The seed is exhausted with boiling alcohol, the solution evaporated, and the fatty residue extracted with water; or the powdered seeds are directly extracted with boiling water, in which case most of the fat is conveniently first pressed out hot. The aqueous solution is then treated with lead acetate and filtered, and the filtrate, after removal of excess of lead by means of hydrogen sulphide, is concentrated, when crystals of impure picrotoxin separate. These are purified by successive crystallisations from water and from boiling strong alcohol. Sometimes the seed is extracted with light petroleum in the place of alcohol (Marck, Arch. Pharm. [iii.] 26, 269).

According to Barth and Kretschy (Sitz. Ber. 81, 7; Ber. 13, 1243), crude picrotoxin is a mixture of three compounds—picrotoxin, picrotin, and anamirtin—which are separated by fractional crystallisation from water and from benzene. This is, however, disputed by Paternò and Oglialoro-Todaro (Gazz. chim. ital. 10, 36; 11, 49; Ber. 14, 539), who regard the compounds named as decomposition products of a perfectly definite picrotoxin. Retaining the term picrotoxin for the original substance these chemists propose picrotoxinin as a name for the picrotoxin of Barth and Kretschy. The decomposition of picrotoxin is thus explained: $C_{30}H_{34}O_{13}$ (picrotoxin)$=C_{15}H_{18}O_7$ (picrotin of B. and K., previously called hydrate of picrotoxide by P. and O.) $+C_{15}H_{16}O_6$ (picrotoxinin of P. and O., picrotoxin of B. and K.). The conclusions of

Paternò and Oglialoro-Todaro are supported by the investigations of Schmidt and Löwenhardt (Ber. 14, 817) and Schmidt (Annalen, 222, 313), whilst Barth and Kretschy have replied maintaining their original view (Monatsh. 5, 65). Meyer and Bruger (Ber. 31, 2958) also have come to the conclusion that the picrotoxin of Paternò and Oglialoro-Todaro and of Schmidt is not a definite compound. These investigators find that the recrystallised commercial compound is merely a mixture of picrotoxinin and picrotin in definite, but not molecular proportions, namely 54–55 p.c. of picrotoxinin and 45–46 of picrotin. It may be partially separated into the two constituents by boiling with benzene or chloroform or by treatment with barium hydroxide (*cf.* Angelico, Gazz. chim. ital. 36, ii. 645), or with bromine water, but compare Sielisch (Annalen, 1912, 391, 1) who regards picrotoxin as a loose definite molecular compound.

Recrystallised commercial picrotoxin, the *picrotoxin* of Paternò and Oglialoro-Todaro and of Schmidt, consists of brilliant rhombic prisms, which melt at 199°–200° (Sch.). It is intensely bitter and poisonous. It is very soluble in hot water, alcohol, or benzene, and sparingly so in ether or chloroform.

By the addition of bromine water to a hot aqueous solution of picrotoxin, monobromopicrotoxinin separates, and on evaporating the filtrate, picrotin is obtained, and can be purified by repeated extraction with small quantities of hot chloroform and recrystallisation from water (M. and B.). *Picrotin* $C_{15}H_{18}O_7$ forms small felted needles or thick rhombic prisms, m.p. 248°–250°, which are readily soluble in absolute alcohol or acetic acid, but only sparingly so in ether, chloroform, or benzene. It reduces Fehling's solution and ammonio-nitrate of silver. It possesses a bitter taste, but is not poisonous. *Benzoylpicrotin* $C_{15}H_{17}O_7Bz$ forms colourless needles, m.p. 236°; a *dibenzoyl derivative*, m.p. 247°–248°, is obtained by the action of benzoyl chloride at 190°. *Acetylpicrotin* $C_{15}H_{17}O_7Ac$, m.p. 244°–245°, is probably identical with the compound described by Paternò and Oglialoro-Todaro as diacetylpicrotoxinin. When warmed with fuming nitric acid, picrotin yields a nitro derivative *anhydronitropicrotin* $C_{15}H_{15}O_6NO_2$, m.p. 260° (M. and B.). On oxidation, two isomeric acids $C_{15}H_{18}O_8$, are obtained *α-picrotinic acid*, m.p. 245°, and *β-picrotinic acid*, m.p. 254° (Angelico, Gazz. chim. ital. 39, i. 296; 40, i. 391; 41, ii. 337; Atti R. Accad. Lincei, [v.] 19, 1, 473). Phosphorus pentachloride acts as a dehydrating agent on picrotin converting it into *anhydropicrotin* $C_{15}H_{16}O_6$, m.p. 317° (decomp.), which differs from picrotin by not reducing Fehling's solution (Horrmann, Ber. 1910, 43, 1903). *Picrotoxinin* $C_{15}H_{16}O_6,H_2O$, the 'picrotoxin' of Barth and Kretschy, is best obtained by the reduction of bromopicrotoxinin with zinc and acetic acid. Picrotoxinin crystallises in rhombic tables, which become anhydrous at 100° and melt at 200°–201°. It is bitter and exceedingly poisonous. It dissolves readily in hot water, benzene, alcohol, ether, or chloroform; it is also soluble in alkalis, but is not reprecipitated on the addition of acids. Sulphuric acid develops an intense orange-red coloration, and when hydrogen chloride is led into an ethereal solution of the compound polymerisation occurs and *picrotoxide*, m.p. 308°–310°, is formed. *Bromopicrotoxin* $C_{15}H_{15}BrO_6$ is most readily obtained by adding bromine water to a hot nearly saturated aqueous solution of picrotoxinin until the solution remains permanently yellow. It separates from absolute alcohol in glistening needles, m.p. 259°–260°. With benzoyl chloride it yields a crystalline benzoyl derivative, which melts at 237°–238° (Sch.). On reduction by hydriodic acid and phosphorus both picrotin and picrotoxinin yield *picrotoxic acid* $C_{15}H_{18}O_4$, m.p. 134°, and also a *ketone* $C_{14}H_{16}O_3$ (Angelico; Oglialoro-Todaro and Forte, Gazz. chim. ital. 21, ii. 213). Angelico (Gazz. chem. ital. 1912, 42, ii. 590) has given (very) provisional formulæ for picrotoxinin and picrotin. Horrmann (Ber. 1912, 45, 3434; 1913, 46, 2793; 1916, 49, 2107; Annalen, 1916, 411, 273; Horrmann and Behschnidt, Arch. Pharm. 1921, 259, 69) agrees with Angelico's formulæ in so far as picrotoxinin and picrotin are both dilactones; in addition the former has two and the latter three hydroxyl groups. Hot or cold alkalis split off acetone. *Anamirtin* $C_{18}H_{24}O_{16}$ occurs in small proportion in the seed, and collects in the aqueous mother liquors in the preparation of picrotoxin. It is distinguished by its sparing solubility in chloroform and benzene. It is not bitter, is not poisonous, and does not reduce Fehling's solution or ammonio-nitrate of silver. When heated, it chars, without melting, at 280° (Barth and Kretschy).

Cocculin $C_{19}H_{26}O_{10}$ is another constituent of the seed, discovered by Löwenhardt (Annalen, 222, 353), and occurs only in small proportions. It is found in the alcoholic mother liquors in the preparation of picrotoxin. It crystallises in needles, is difficultly soluble in hot, and insoluble in cold, water, alcohol, or ether, and does not give the colour reactions of picrotoxin.

For the detection of picrotoxin in beer the chemical reactions are not of much use. Extracts are prepared from neutral or acid solution by means of ether, chloroform or amyl alcohol, which are tested physiologically (*cf.* Langley, Amer. J. Sci. [ii.] 34, 109; Schmidt, J. 1862, 629; Köhler, J. 1868, 796, 893; Blas, J. 1872, 936; Depaire, J. 1872, 946; Palm, Zeitsch. anal. Chem. 24, 556; Christoni, Arch. Farmacol. Sperim. 1912, 13, 220; Chem. Soc. Abstr. 1913, i. 140; and Allen's Commercial Organic Analysis, 1913, vii. 160). G. B.

PICROTOXININ *v.* PICROTOXIN.

PICRYL BROWN. A colouring matter belonging to the class of yellow, orange-yellow, and brown dyes introduced by Nölting and v. Salis-Mayenfeld, and obtained either by sulphonating nitro derivatives of secondary and tertiary aromatic amines, or by the action of such compounds as dinitrochlorobenzene, trinitrochlorobenzene (picryl chloride), chlorotetranitronaphthalene, &c., on the sulphonic acids of aromatic amines (D. R. P. 22268 of Aug. 31, 1882, expired Jan. 1887; W. J. 1883, 545). It is prepared (1) by sulphonating trinitrodiphenylamine (*cf.* Townshend, Ber. 7, 1249) with $2\frac{1}{2}$ times its weight of 40 p.c. anhydrosulphuric acid, or with 5 times its weight of sulphuric acid of 66°Bé.; or (2) by boiling a concentrated aqueous solution of 3 parts sulphanilic acid, 3 parts picryl chloride, and $2\frac{1}{2}$ parts of

sodium acetate. Picryl brown is soluble in water, and in an acid bath dyes silk and wool yellow.

PIGMENTS (*L. pigmentum*, from *pingere*).

Definition.—Insoluble coloured powders yielding paints when admixed with suitable media. This definition excludes dyes or stains, which are soluble in the vehicles used.

History.—The use of pigments can be traced back to remote antiquity, even to palæolithic times. Thousands of years before the Christian era, the ancient Egyptians excelled in pictorial art. In Assyria, in Lydia, from the eighth century B.C., and by the Ionians and Phocæans, from about the sixth century B.C., painting was skilfully practised and held in high esteem. Cimon of Cleonae, his successors Polygnotus of Thasos (463 B.C.), Apelles of Colophon, and Zeuxis of Heraclea, and other early painters worked chiefly in fresco and tempera, with a limited range of pigments, nearly all mineral. Encaustic was not commonly practised until after the time of Alexander the Great. The pigments were mostly the ochres, red lead, cinnabar, orpiment, chalk, gypsum, lapis lazuli (?), indigo, carbon, and certain special colours, such as 'Egyptian blue' (a copper fritt or glass) and 'Tyrian purple.' From the accounts given by Pliny the Elder and Theophrastus, it would appear that a blue prepared from lapis lazuli was not known in classical times. Red lead, or minium, was used for the coloured statue of Jupiter, set up by King Tarquinius Priscus in the Roman Capitol. The vegetable colours anciently used have probably for the most part decayed, leaving no traces; but a pink madder lake and a yellow lake have been discovered among the pigments of the ancient Egyptians. Until quite recent times, artists prepared and ground their own pigments; this work is now almost invariably done by the colour manufacturer.

Properties.—Pigments must be durable; insoluble; inert, *i.e.* unaffected by one another; in general indifferent to the media; of good body and covering power; easy to manipulate with vehicles on the palette, and of a fine shade of colour. Certain pigments, when used in oil paints, possess the additional property of facilitating the drying of the oil with which they are mixed: white lead is a conspicuous example. The characteristics here laid down are those usually desired; but there are exceptions in the case of pigments used in art. Thus some of the colours most valued by artists possess considerable transparency; in water-colour work the conditions of drying are altogether different from those in oil-painting.

In regard to durability or permanence, an ideal pigment should be fast to light, unchanged by exposure to the atmosphere and moisture, proof against the action of acids or alkalis, and unaffected by sulphur compounds, such as hydrogen sulphide or carbon disulphide. Of the large number of pigments known, comparatively few fulfil all these requirements. In particular circumstances, especial qualities become necessary: thus, for decorative and fresco work, pigments must be fast to lime, for ceramic use they must be proof against fire, and if the paintings have to be lacquered, they must be fast to varnish.

By some authorities the term 'permanence' is restricted to unalterability of hue, and 'durability' to the conservative effect of a pigment upon the surface which it covers. Pigments unchanged by admixture with other colours are said to possess inertia. Covering power and body are not convertible terms. Spreading or covering power applies to the capability of being extended or spread over a large surface, and may be measured by the number of sq. cms. of surface which can be covered by one gram of pigment, so that the covered surface will not show through. With decreasing size of particles the covering power increases to a maximum and diminishes when the size of the particles approaches the wave length of the visible light waves (Kolloid Zeitsch. 1915, 16; Reports of the Progress of Applied Chemistry, 1916, 184). Body refers to opacity.

The opacity or hiding power of a pigment is greater the greater the degree of fineness up to a certain limit, the higher the refractive index, and the smaller the amount of oil absorbed by the pigment, which latter condition is of great practical importance (H. A. Gardner, J. Ind. Eng. Chem., 1916, 8, 794).

The light reflecting values of paints have been measured and it has been pointed out that oil paints have higher coefficients than water paints, those with traces of yellow giving the best reflection, and among colours fatal to good reflection are traces of black, red, blue, and deep yellow. The effect of pigments on the temperature of objects upon which they are laid has also been determined (H. A. Gardner, J. Franklin Institute, 1916, 181, 99; L. Bell, Elec. World, 1915, 65, 211; *see also* G. W. Thompson, J. Ind. Eng. Chem. 1913, 5, 120).

Origin, classification, and characteristics.—The majority of pigments, whether artificially prepared, or obtained almost directly from natural sources, such as the ochres and other coloured earths, are of mineral or vegetable origin. A few, such as sepia, purree, mummy (sometimes), and the preparations derived from the several species of *Coccus*, are animal products.

The native earths are levigated, dried, sifted, graded, ground and, in certain cases, calcined. Most artificially prepared pigments are manufactured by wet precipitation methods: instances are chrome yellow, Prussian blue, and antimony vermilion. In a large number of cases, however, dry processes and various temperatures are required; *e.g.* artificial ultramarine, vermilion, and ivory black. Lakes are made by precipitating organic colouring matters, which may be of vegetable or animal origin, and at the present time are frequently so-called coal-tar colours, in conjunction with alumina, lime, and the like. Special methods are employed in the manufacture of certain pigments, such as white lead.

The classification of the mineral pigments, adopted in this article, strictly follows the ordinary grouping of the metals present, as they are separated in analysis. Silicious and carbonaceous pigments follow, and organic colouring matters are described last. When possible the colours follow in the order: white, yellow, red, green, blue, brown, and black.

Pigments containing mercury. Three mercury pigments only will be included in the following summary:—

Vermilion, cinnabar, zinnober, mercuric sulphide, HgS: a brilliant colour, usually prepared from its elements, which are at first caused by

simple attrition, or other means, to combine into a black mass, called 'ethiops,' chiefly amorphous mercury sulphide, together with free sulphur. The molecular change into the scarlet sulphide is effected by sublimation, treatment with alkalis, alkaline polysulphides, or the like.

Numerous other methods of manufacture have been suggested and practised. Vermilion possesses great opacity, but dries imperfectly in oil and is liable to separate from the vehicle used. It is permanent in oil, durable in tempera and fresco, but changeable in water colour by the influence of the solar rays. Hydrogen sulphide does not affect it, and in oil it can be mixed with all except certain copper pigments. As it is a volatile compound, it is ineligible for enamels and ceramic ware.

Brilliant scarlet, *Royal scarlet*, *Pure scarlet*, mercuric iodide, HgI_2: extremely brilliant as a pigment and of good body, but fugitive in oil, useless in water colour, immiscible with many purposes.

Pigments containing lead. Of high importance among the lead pigments and, indeed, among commercial pigments generally, is *white lead*, called also *Krems* or *Kremnitz white*, *Berlin white*, *Silver white*, *Cerussa alba*, *Céruse*, *Bleiweiss*, *Blanc de Plomb*, *Blanc d'argent*, and *Flake white*, $2PbCO_3,Pb(OH)_2$. This basic carbonate of lead is one of the most rapidly drying pigments commonly used in oil; it possesses great opacity and covering power, and is facile in working. Miscible with most durable colours, it promotes the drying of many which have slight siccative qualities of their own. Unfortunately, white lead is highly poisonous, its manufacture is attended with risk to the operatives, it is readily discoloured by hydrogen sulphide, and used with oil it emits a nauseous odour. Substitutes have been proposed, of which perhaps lithopone, zinc oxide, 'non-poisonous white lead,' antimony oxide, and titanium oxide are the best known.

'*Non-poisonous white lead*,' or *patent white lead*, and '*sublimed white lead*' are composed chiefly of lead sulphate, with small proportions of lead and zinc oxides. The last-named is a basic sulphate with some zinc oxide. These products are little affected by hydrogen sulphide, and are virtually non-poisonous; but the covering power of a lead sulphate pigment is less than that of white lead, and the drying quality is inferior.

Lead oxychloride $PbCl_2.PbH_2O_2$, sometimes called *Pattinson's white lead*, is very rarely used as a white pigment, as also have been the normal carbonate, sulphite, hydroxide, and other salts of lead. All are less satisfactory than the basic carbonate.

Turner's yellow, *Cassel yellow*, *Montpellier yellow*, or *Verona yellow*, $PbCl_2,7PbO$, is another basic lead chloride, now superseded by chrome yellows.

Massicot and *litharge* are, respectively, yellow and red modifications of lead monoxide, PbO. The monoxide is now scarcely used as a pigment, but as a drier is of considerable importance. Large quantities are used by potters, glassmakers, and rubber manufacturers.

Red lead, *Orange lead*, *minium*, *mennige*, *Paris red*, Pb_3O_4, sometines Pb_4O_5, a fine orange-red pigment, which very quickly dries in oil but is discoloured by hydrogen sulphide, and is incompatible in admixture with certain sulphur-containing pigments, such as lithopone and cadmium yellow. As a priming coat, in conjunction with white lead for ordinary work, it is extremely useful. *Orange mineral* is a less dense form of red lead.

Sublimed blue lead is a mixture of basic sulphate, $2PbSO_4{\cdot}PbO$, with lead sulphate, sulphite, oxide, and carbon. It is used to a considerable extent as a protective pigment.

Pigments containing copper. *Vandyke red*, copper ferrocyanide, Cu_2FeCy_6, is a brownish-red pigment, occasionally used in artistic painting, but it is untrustworthy and liable to darken.

Vert de Gris, *Verdigris*, *Vert de Montpellier*, *Grünspan*, basic copper acetate, varies in hue according to the basicity of the compound. Green verdigris, of the brightest tint, is $2Cu(C_2H_3O_2)_2{\cdot}CuO,6H_2O$; blue verdigris is $Cu(C_2H_3O_2)_2.CuO,6H_2O$: but other basic acetates are known and the commercial pigment is a variable mixture of several of these salts. It is made by the action of acetic acid upon copper in the presence of air and moisture. This pigment is useless in water-colour painting, injured by hydrogen sulphide, carbon dioxide, and moisture, immiscible with sulphide and some other pigments, and is a powerful poison. In oil it dries well, but is only permanent if 'locked up' by the presence of a large quantity of a resinous varnish.

Mountain green, *Green verditer*, *Malachite*, *Mineral green*, or *Berggrün*, the natural green hydroxycarbonate of copper, $CuCO_3{\cdot}Cu(OH_2)$. This is the mineral malachite, finely ground, and is known to have been used by the Græco-Roman artists. As an oil-paint it is moderately durable, but it is liable to darken and assume a brownish or olive tint, and for water-colour it is unsuitable. It will blacken if mixed with cadmium yellow, ultramarine, &c., and is highly sensitive to hydrogen sulphide.

Schweinfurt green, *Mitis green*, *Vert Paul Véronèse*, *Vert de Paris*, *Emerald green*, cupric aceto-arsenite $Cu(C_2H_3O_2)_23(CuAs_2O_4)$, is an exceedingly fine but very poisonous colour, prepared by heating together verdigris, water, and arsenious oxide, the precipitate formed being washed and dried. Its manufacture is one of the most difficult problems in colour making. The chief difficulty is to allow the green a sufficient time for undisturbed crystallisation, since on this the brightness of the shade primarily depends. Inadvisable for use as a water-colour, it is durable in oils, but must not be mixed with sulphide pigments, such as cadmium yellow and ultramarine, nor exposed to hydrogen sulphide, which quickly darkens it. Emerald green is somewhat deficient in body and dries slowly. It is not trustworthy for tempera or fresco work.

Scheele's green a basic copper arsenite, varying somewhat in composition, is a pale green pigment of an extremely poisonous character, and is now seldom used. Hydrogen sulphide and sulphide pigments are even more injurious to it than to Schweinfurt green.

Brunswick green was formerly basic chloride of copper, $CuCl_2{\cdot}3CuO,4H_2O$, now not used as a pigment. The name is now applied to a mixture of Prussian blue, chrome yellow, and barytes.

Mountain blue, Blue verditer, Chessylite, Azurite, Blue ashes, or *Bergblau*, the natural blue hydroxycarbonate of copper, $2CuCO_3 \cdot Cu(OH)_2$. Both this and the green hydroxycarbonate (above described) have been artificially manufactured, but not with conspicuous success. Blue verditer is not permanent, and is a pigment little used, artificial ultramarine and cobalt having superseded it.

Lime blue and *Bremen blue* are essentially copper hydroxide, $Cu(OH)_2$, associated with calcium sulphate and copper carbonate respectively: both were formerly much used in decorative work. Blue lakes from coal-tar dyes and artificial ultramarine have virtually driven these pigments off the market.

Stannate, phosphate, borate, silicate, and other salts of copper have been tried as pigments, but not very successfully.

Pigments containing cadmium. *Cadmium yellow, pale cadmium, orange cadmium, Orient yellow, radiant yellow, aurora yellow*, &c., are cadmium sulphide, CdS. The cadmium pigments, if free from uncombined sulphur, may safely be mixed with white lead in oil; and, being themselves unaffected by hydrogen sulphide, they hinder the darkening of flake white by that gas. Light, air, and moisture have little effect upon the pure cadmium colours when used in oil-painting, but the paler shades are extremely fugitive in water-colour, and the presence of free sulphur is very detrimental since it enhances the tendency to fade. Cadmium pigments are entirely incompatible with the copper greens and blues, and exert a darkening action upon Naples yellow, chrome yellow, Cassel or Turner's yellow, and the like.

Neutral orange, Penley's neutral orange, is a mixture of cadmium sulphide with Venetian red.

Pigments containing bismuth. Bismuth oxychloride, 6BiOCl,Aq., or $[2(BiCl_3 \cdot Bi_2O_3)H_2O]$, is called *pearl white*, a name which has also been applied to indigo-tinted flake white.

Pigments containing antimony. *Antimony white*, antimonious oxide, Sb_4O_6, finds employment as a substitute for flake white, *v.* PAINTS. In oils, especially, this pigment is durable and trustworthy. Another antimony white is *powder of algaroth* $Sb_4O_6 \cdot 2SbCl_3$.

Antimony yellow, true *Naples yellow, Jaune d'Antimoine, Giallo di Napoli*, is basic lead antimoniate, PbO,Sb_2O_5, and was usually prepared by heating together potassium antimonyl tartrate (tartar emetic), lead nitrate and sodium chloride. As a painter's colour Naples yellow is obsolete and has been replaced by the chromes. Naples yellow, or an allied antimonial yellow, has been used for many centuries in enamels and pottery ware. It is unsuitable for water-colour painting. Several imitations of this pigment are, or have been, in the market: one is a mixture of cadmium yellow with zinc white; another was a variety of yellow ochre (Church).

Antimony vermilion, antimonzinnober, antimonious sulphide, Sb_2S_3, or oxysulphide, $2Sb_2S_3,Sb_2O_3$, is a fine red pigment of satisfactory covering power but limited application, owing to its sensitiveness to dilute alkalis and acids. The methods of manufacture are based upon the interaction of the alkaline or alkaline earth thiosulphates and antimonious chloride. An orange-coloured variety of this pigment, *antimony orange*, is made by using hydrogen sulphide as the precipitant.

Pigments containing arsenic. Those in which arsenic is associated with copper have already been considered. There remain the arsenic sulphides:—

King's yellow, Royal yellow, arsenic yellow, auripigmentum, orpiment, arsenic trisulphide, As_2S_3, a brilliant, but fugitive and extremely poisonous pigment, immiscible with lead, mercury, and copper compounds, and now almost entirely superseded by the chromium colours. It is prepared either by precipitation or sublimation.

Arsenic red, arsenic orange, realgar, arsenic disulphide, As_2S_2. This pigment, prepared by a fusion and sublimation-method, is also highly poisonous and generally unsuitable for artists' use.

Pigments containing tin. *Tin white*, stannic hydroxide or orthostannic acid, $Sn(OH)_4$, is used in enamel- and glass-making, but scarcely at all for ordinary decorative or artistic work. To a very considerable extent it has taken the place of bismuth subnitrate and oxycarbonate as a face-pigment.

Mosaic gold, aurum musivum or *mosaicum*, '*Bronze powder*,' stannic sulphide, SnS_2, a lustrous yellow scale-preparation, made by heating a mercury-tin amalgam together with sulphur and ammonium chloride; or a mixture of tin monosulphide, SnS, with mercuric chloride is heated. Another 'bronze' is prepared by fusing together stannic oxide and sulphur. A fused mixture of tin and bismuth, to which mercury is added before the liquid has cooled, yields a silver-tinted metallic pigment.

Other compounds of tin, such as 'tin salt' (stannous chloride $SnCl_2$), stannic chloride $SnCl_4$, 'pink salt' $SnCl_4 \cdot 2NH_4Cl$, and sodium stannate $Na_2SnO_3,3H_2O$, although not pigments, are largely used in the manufacture of the lake-colours.

Pigments containing gold. The use of finely divided metallic gold, whether in the form of leaf, or otherwise, by mediæval artists, monkish scribes, and others, in pictures and illuminated manuscripts, also in the colouring of crimson glass, is well known.

Cassius' purple, gold stannate
$Au_2SnO_3 \cdot SnSnO_3,4H_2O$ or $Au_2,3SnO_2$
is used in glass-ware and ceramic art.

Pigments containing titanium. White pigments that will form rust-preventing paints may be obtained by mixing finely divided titaniferous iron ore (ilmenite) with sulphuric acid and subsequently heating. Various shades of colour may be produced by carrying out the calcination in the presence of air, sulphur dioxide or other gases, whilst the temperature has also an influence upon the colour (Bulletin of Imp. Inst. 1922, 20, 350, and *v.* PAINTS.

Pigments containing aluminium. The *metal*, finely powdered, now receives a wide application as the pigmentary constituent of aluminium paint.

Kaolin, China clay, hydrated aluminium silicate, $Al_2O_3 \cdot 2SiO_2,2H_2O$, is durable and practically unalterable as a pigment. In oils, it is somewhat deficient in covering power, but in water-colour and tempera painting it is a very serviceable white pigment, and may fulfil the function of a 'filler.' Thus, a 'Chinese white' for water-colour painting, may contain 3 parts of kaolin to 1 part of zinc oxide. The process of

manufacture consists in levigating and drying the natural clay, the main impurities in which are flakes of undecomposed mica and crystals of quartz. Kaolin is much used in the manufacture of paper, and it is an inexpensive carrier for lake-pigments.

Alumina $Al_2O_3,3H_2O$, though not used as a pigment alone, is a component of many lakes, and occasionally forms part of various composite white pigments, such as satin white, *blanc fixe*, and the like.

Ultramarine, Bleu d'Outremer, one of the most permanent, trustworthy, and beautiful of pigments, was formerly obtained exclusively from the rare and costly mineral *lapis lazuli*, a variety of hauyne, by an elaborate and tedious elutriation method. The chief constituents of ultramarine are alumina, soda, silica, and sulphur. The formula is doubtful, but may be $Na_4(NaS_3Al)Al_2(SiO_4)_3$ (Brögger and Backström). L. Bock (J. Soc. Chem. Ind., 1915, 561) states that the grouping of Na, Al, and SiO_2 in the ultramarine molecule is similar to that in zeolites, because of its formation from them by treatment with alkali sulphides. The state of combination of sulphur in the various products is still doubtful. He concludes that ultramarines rich in silica approximate to double silicates, those rich in alumina to aluminium silicates, and that sodium is less readily replaced in the double silicates than in aluminium silicates. The existence of isomeric ultramarines containing —SNa or —SONa groups attached to Al or Si respectively is considered probable. In 1828, Guimet succeeded in manufacturing artificial ultramarine, a pigment little inferior to the natural product of the same composition, equally permanent both in oil and water-colour painting, and moderate in price. Several varieties of artificial ultramarine are made : sulphate ultramarine, which possesses a pale greenish-blue shade ; soda ultramarine, poor in silica, the purplish-blue product most in use ; and soda ultramarine, rich in silica, a pigment mostly used by paper-makers. A higher burning temperature can be used with mixtures rich in alumina than with those rich in silica. *Lime green* or *green ultramarine* is the first stage in the manufacture, and is the colouring ingredient of green water-paints. By roasting with sulphur, green ultramarine is 'coloured,' *i.e.* it is caused to assume the azure tint. Other varieties of ultramarine than those mentioned are *red*, *violet*, and *yellow ultramarine*. The raw materials used in making artificial ultramarine are kaolin, silica, soda, carbon, sulphur, and sodium sulphate. *Mineral grey* and *ultramarine ash* are grey or bluish-grey residual products from the processes of treatment of the mineral *lapis lazuli*.

Ultramarine violet is obtained when the soda blue is heated with sal ammoniac for many hours at a temperature of about 150°. Further heating with steam and hydrochloric acid converts the violet pigment into *ultramarine red*, *v.* ULTRAMARINE.

Pigments containing iron. *Yellow ochre, mineral yellow, Roman ochre, Oxford ochre, stone yellow, brown ochre, golden ochre, Chinese yellow*, &c., are silicious and argillaceous earths, often containing as impurities lime, barium, and other metallic salts, but all owing their yellow or brown colour to the presence of hydrated ferric oxide. These colours, which are prepared for the market by careful sampling and elutriation, are mined in many parts of the world, are exceedingly lasting, have no effect upon other pigments, are not injured by light or by impure atmospheres, and they can be used with any medium. Ochres vary in opacity, as they vary in composition : most of them possess fair covering power. Pigments of this class were used by the ancient Egyptians, Assyrians, Greeks, and Romans.

Raw Sienna, Terra di Siena, Italian earth, is a browner-tinted, manganiferous yellow ochre, occurring in Tuscany, in the vicinity of Rome, Cyprus, and elsewhere. Some American siennas are of very serviceable quality. Raw sienna is fitted for oil, water-colour, tempera, and fresco-painting.

Burnt Sienna is a pigment of an orange-brown tint, permanent and suitable for every sort of artistic work. It is made by cautiously calcining raw sienna.

Red ochre, Scarlet ochre, Red chalk, Ruddle, Bole, sinopis, Terra rosa, &c., are varieties of the native anhydrous ferric oxide, or red hæmatite, Fe_2O_3. All are durable pigments and good driers.

Indian (or *Persian*) *red* is, in strictness, a native product (also hæmatite), of a somewhat purplish shade, imported from the East. But the so-called *Indian red* is manufactured by calcining ferrous sulphate (copperas, or green vitriol), $FeSO_4,7H_2O$.

The colours of the red varieties of ochres are not so rich as those obtained by calcining the yellow varieties. The best yellows do not always produce the best reds, the length of heating and rate of cooling influencing the final shade, but all shades produced by calcination are stable.

Light red, Burnt ochre, Brun rouge, also, is calcined yellow ochre. The period of heating is 10 hours. This pigment is an opaque, permanent, and innocuous colour, of a scarlet tint, tempered by shades of brown and grey.

Venetian red, Colcothar, Caput mortuum vitrioli, Crocus, Rouge. The natural pigment known as Venetian red is a variety of red hæmatite, of a purer red than either *light red* or *Indian red*, but the artificial products are obtained by calcining copperas, or the ochres. Time, in the case of the ochres, about 8 hours ; temperature, between 100°–250° the colour gradually changes to yellowish-brown, and at 250° suddenly becomes red. Further heating to 700°–800° gives a reddish-purple ochre, but if the mass is gradually heated to above 950° it reverts to its original yellow with different properties : this variety is obtained only within narrow temperature limits of about 50°, as further heating causes the ochre to blacken. If pure, Venetian red is uninjurious to other permanent colours, but soluble salts, especially sulphates and traces of acid, must be absent. The last-named exert a detrimental action upon organic pigments, such as indigo ; upon the vehicle used ; and also on the surface coated, if this chance to be of metal.

Prussian brown, a rarely used pigment consisting of ferric oxide in admixture with carbon and made by carefully calcining Prussian blue. It is permanent and a good drier.

Yellow to brown pigments of good covering power are obtained by the atmospheric oxidation

of hydrated sulphide of iron, preferably in presence of moisture, *e.g.* waste ferrous chloride solution from the pickling of iron is treated with barium sulphide solution, and the precipitated iron sulphide is oxidised by means of air, filtered off and washed. The free sulphur may be removed by a suitable solvent if desired.

Mars yellow, Mars orange, Mars red, Mars brown, and *Mars violet.* These are artificial ferruginous pigments, prepared by precipitating salts of iron, with or without the addition of alum, by milk of lime or an alkaline hydroxide, drying, and calcining the precipitates at various temperatures, according to the colour required. The Mars pigments present no particular advantages over the ordinary iron yellows and reds, and they may be somewhat injurious to certain of the madder pigments.

Terre verte, Verona green, Veronese earth, Green earth, &c., are pale, bluish-green, natural pigments, consisting essentially of an alkaline and magnesian ferrous silicate; but as the localities are numerous, considerable variations in composition are observed. *Terre verte* is one of the most inert and permanent pigments used by artists, but though deficient in body and intensity of hue, it is important, as it absorbs and fixes basic dyes. It is available for painting in oil, water-colour, tempera, and fresco.

Prussian blue, Chinese blue, Antwerp blue, Berlin blue, Paris blue, soluble blue, bronze blue, Saxon blue, &c. This pigment occurs in several forms. Commonly, it is a mixture of potassium ferric ferrocyanide, $K_2Fe_4Cy_{12}$, with ferric ferrocyanide, Fe_7Cy_{18}; but the most permanent form is ferric ferrocyanide, Fe_7Cy_{18}. The presence of $FeFe(CN)_5CO$ imparts a violet tinge to the finished blue. The large variety of shades of Prussian blue are due to conditions of temperature and concentration of the solutions and to the method and extent of the oxidation. Some of the varieties named, such as Antwerp blue and Paris blue, contain other ingredients and are inferior to the true Prussian blue, which is an intense colour with a slight greenish shade, is permanent, miscible with other pigments and useful both in oils and water-colour. L. Bock (J. Soc. Chem. Ind., 1916, 610) considers that the distinction between Paris and Prussian blues is founded upon the purity of the colour, which depends upon the quality of the substances used in manufacture. This pigment is not available for fresco-work or enamels. Though liable to fade in a strong light, it recovers its intensity of hue when kept for a while in the dark.

Pigments containing chromium. *Chrome yellow,* normal lead chromate, $PbCrO_4$, is a salt of a full yellow hue, prepared by a simple precipitation process. Usually mixed or diluted chrome yellows are met with in commerce, lead sulphate, barium sulphate, or gypsum, being associated with the lead chromate: examples are $PbCrO_4 \cdot PbSO_4$ and $PbCrO_4 \cdot 2PbSO_4$. *Cologne yellow* consists of lead chromate and sulphate, sometimes with calcium sulphate. *Paris yellow* is a mixed 'chrome' of a somewhat similar type. Other products are *primrose chrome, pale chrome, middle chrome,* and *deep chrome.* The various shades can be obtained by varying the conditions, temperature, concentration, and time. An excess of lead acetate should be used so as to ensure absence of potassium chromate from the product which would rapidly convert the lead sulphate (necessary for any particular shade) into lead chromate (J. Milbauer and K. Kohn, J. Soc. Chem. Ind., 1916, 35, 972). These colours are far from permanent, being sensitive to the action of hydrogen sulphide, darkened in admixture with sulphide pigments, and liable to change in the presence of reducing substances. For water-colours and distemper (tempera) painting, the yellow chromes are quite unsuitable. In oils, they are permissible, with certain limitations.

Zinc chrome, Citron yellow, zinc chromate, $ZnCrO_4$, is a pale yellow pigment of fairly good covering power, less used alone than for associating with Prussian blue in the production of various shades of mixed greens. The composition of this pigment is sometimes represented by the formula $3(ZnCrO_4),K_2Cr_2O_7$. L. Bock (Kolloid Zeitsch., 1917, 20, 145) reviews the properties of the various basic zinc chromates and the alkali zinc chromates described in the literature with reference to the use of zinc yellow in the pigment industry. Zinc chrome is not affected by hydrogen sulphide, and is miscible with most other pigments without deterioration. Acids, alkalis, and organic compounds attack it, the last-named having a tendency to change the colour from yellow to green.

Lemon chrome, Lemon yellow, Baryta yellow, Barium chrome, permanent yellow, yellow ultramarine, Steinbüller yellow, and *Jaune d'Outremer,* are names given to barium chromate, $BaCrO_4$, the most stable of the chromium pigments. Prepared by the double decomposition of barium chloride and potassium chromate, filtering, washing, drying, and grinding, lemon yellow is obtained as a very pale, moderately opaque, and serviceable pigment, which can be used with safety in oils and fresco. For water-colour painting it is less suitable, the yellow assuming a greenish hue under unfavourable conditions of exposure. The greatly inferior *strontian yellow,* strontium chromate, $SrCrO_4$, is not infrequently substituted for baryta yellow.

Lime chrome, calcium chromate, $CaCrO_4$, is a similar pigment of little value.

Siderin yellow, basic ferric chromate, $Fe_2(CrO_4)_3$, is a somewhat pale-hued product, very stable, useful in stereochromy (water-glass painting), and of occasional application in water-colour work.

Copper chromate $CuCrO_4$ is a red salt, somewhat dull in hue, which has been proposed and actually used as a pigment, but it is fugitive and of little practical value. The equally unserviceable mercury and silver chromates have already been mentioned (*v. supra*).

Chrome red, Austrian cinnabar, Orange chrome, Derby red, Chinese red, &c., basic lead chromate, $PbCrO_4,PbO$ or $Pb_2CrO_4(OH)_2$, is an orange-scarlet pigment, made by heating normal lead chromate with a dilute solution of sodium or potassium hydroxide. The shade obtained depends upon the extent to which the reaction proceeds. Like the yellow chromes, the chrome reds are incompatible with sulphide pigments, such as cadmium yellow and ultramarine, and they are liable to turn green in the presence of reducing substances, such as oxidisable organic pigments. But, unlike the yellows, they may be used with caution in tempera work.

Chrome green, Vert de chrome, true chrome green. Prepared by (*a*) igniting ammonium dichromate, (*b*) heating together potassium chromate and sulphur, (*c*) the ignition of a mixture of potassium dichromate, ammonium chloride, and sodium carbonate, (*d*) adding a solution of sodium phosphate to a neutral solution of chromic chloride. This fine pigment is, or should be, either approximately pure, anhydrous chromium sesquioxide, Cr_2O_3, or (according to the last process of manufacture) chromium phosphate, $Cr_2(PO_4)_2$. Some products are a mixture of the two compounds. The oxide pigments are of finer hue than the phosphate colours. Chrome green is one of the most permanent, generally trustworthy, and widely applicable colours used by artists.

Mixed chrome greens are mixtures of chrome yellow, barium sulphate or gypsum, and Prussian blue. These are greatly inferior to true chrome green and are unstable in the presence of sulphur, lime, alkalis, and oxidisable vegetable or animal pigments.

Viridian, Veridian, Vividian, Guignet's green, Mittler's green, Vert emeraude, hydrated chromium sesquioxide, $Cr_2O_2,2H_2O$, is prepared by calcining a mixture of crystallised boric acid with about one-third its weight of potassium dichromate, treating the residue with hot water, washing, wet-grinding, and drying. One of the most valuable pigments used in art, viridian is universally applicable, without action upon other pigments, and absolutely permanent. Though called, in France, *Vert emeraude*, it is, of course, entirely distinct from the fugitive and poisonous emerald green already described among the copper pigments.

Pigment containing nickel. *Nickel yellow* is a permanent colour, obtained by precipitating a solution of nickel sulphate with sodium phosphate, washing, drying, and igniting.

Pigments containing cobalt. *Cobalt yellow, Aureolin,* cobalto-potassium nitrite

$$K_6Co_2(NO_2)_{12},xH_2O$$

or sodium-potassium-cobalt nitrite

$$K_2NaCo(NO_2)_6,H_2O$$

is a bright yellow, durable pigment which is without action upon other pigments, with the exception of the lakes, and is only very slowly attacked by hydrogen sulphide. Aureolin is permanent in water-colour, as well as in oils.

Cobalt pink, magnesia-cobalt pink, is produced when a thin paste of finely divided magnesium carbonate together with an aqueous solution of cobalt nitrate is dried, and subsequently ignited in a covered vessel at a high temperature. Strongly ignited cobaltous arsenate and phosphate are also of a pink or foxglove-red colour, inclining to violet. These pigments are sometimes known as '*cobalt red*' or '*cobalt violet.*'

Rinmann's green, Cobalt green, sometimes termed *zinc green,* cobalt zincate. CoOZnO, is a delicately shaded and artistically satisfactory pigment, of great permanence, and innocuous to other colours. The best product is obtainable by drying and calcining zinc oxide, previously made into a paste with an aqueous solution of cobalt nitrate, sulphate or chloride. Another cobalt green is prepared by mixing zinc and cobalt solutions with sodium phosphate, and igniting the washed and dried precipitate. The product so obtained has a bluer tint than the true Rinmann's green.

Turquoise green, chrome-alumina cobalt oxide, is a bluish-green pigment mostly used in ceramic painting, but occasionally also in oils. It is made by heating to redness aluminium and chromium hydroxides together with cobaltous carbonate.

Cobalt blue, Thénard's blue, Leyden blue, King's blue, cobalt ultramarine, Gahn's ultramarine, azure blue, &c. Several methods are used in the production of cobalt blue. The variety of this pigment known as Wenzel's blue can be prepared by adding ammonia to a solution of cobalt chloride, mixing the precipitated and washed hydroxide with alumina, drying, and igniting; or by moistening recently precipitated aluminium hydroxide with a solution of cobalt nitrate, drying the mixture, and strongly igniting it. Another cobalt blue is made by mixing freshly precipitated and washed cobalt phosphate with newly precipitated and washed aluminium hydroxide. The mass is dried, ignited, and ground. Cobalt arsenate may be substituted for the phosphate. Also a mixture of alum and cobalt nitrate solutions may be precipitated by sodium carbonate, the precipitate being washed, dried, and ignited, as usual. It will be seen that cobalt blue may be a cobalt aluminate or a compound of the phosphate or arsenate of cobalt with alumina.

These cobalt pigments are permanent, except in the presence of ammonium sulphide. They are available in all media, including fresco, and are without action upon other pigments. The tint of the blue is slightly greenish, and in artificial light a shade of violet is perceptible. Cobalt blue is especially valuable in water-colour, for which it is somewhat more suitable than for painting in oils.

Leitch's blue, or *cyanine blue,* is a 'mixed' pigment, composed of cobalt blue and Prussian blue. It is moderately durable, but presents no very striking advantages. As Prussian blue is a constituent, this pigment cannot be used in fresco work.

Smalt, Saxon blue, cobalt-potassium silicate, is a deeply coloured glass which, in a fine state of division, was at one period much used as a pigment. Artificial ultramarine has, to a great extent, replaced it. Smalt is deficient in chromatic and covering power, but it is perfectly durable and without injurious effect upon any other pigments.

Cœruleum, Cerulean blue, Cœlinblau, Bleu céleste, cobalt stannate, is a greenish-blue, permanent, semi-opaque colour, made by igniting stannic oxide, previously moistened with a solution of cobaltous nitrate. It possesses the advantage of appearing less violet by artificial light than the other cobalt blues.

Cobalt brown results when cobaltous sulphate, ferrous sulphate, and ammonium sulphate, or ammonia alum, are very strongly heated together. Another method of manufacture is to mix ferric oxide with aluminium hydroxide and a cobaltous salt, the mixture being then ignited.

Pigments containing manganese. *Manganese green, Cassel green,* barium manganate, is made by cautiously heating a mixture of manganese nitrate or oxide with barium nitrate. Or, manganese dioxide and carbonate may be heated with barium peroxide. Another manganese

green (Böttger's) is made as follows: A solution of manganese chlorate is precipitated by barium nitrate. The violet compound produced is washed, dried, mixed with barium hydroxide and carefully heated. A green mass results, which requires washing with water and further treatment.

Manganese blue. A mixture of kaolin, manganese oxide and barium nitrate, or of silica, manganese oxide and barium nitrate, ignited at a red heat, is stated to yield a blue product, available for use as a pigment. Soda ash, silica, calcium carbonate, and manganese oxide, mixed together and calcined, yield a similar product.

Manganese violet, mineral violet, permanent violet, impure manganese metaphosphate, is prepared by evaporating to dryness a mixture of solutions of phosphoric acid and manganous chloride, fusing the residue, boiling with ammonium carbonate solution, allowing the turbid liquid to stand, filtering, evaporating the filtrate to dryness, fusing the residue, pulverising it and boiling with water. The pigment separates as a fine violet precipitate, which must be collected on a filter, washed, and dried.

Raw umber, Turkey umber, Levant umber, Terra ombra, is a greenish- to yellowish-brown, silicious and ferruginous earth, containing a considerable proportion of one or other of the higher oxides of manganese, Mn_3O_4 and MnO_2. Most of the best specimens are of Cypriote origin, but many countries yield a supply of this natural pigment, which merely has to be ground, levigated, and dried at 100°. Raw umber is a permanent and justly-valued pigment. It has no injurious effect upon other stable colouring matters.

Burnt umber, Velvet brown, Chestnut brown, &c., result from the calcination of raw umber; they are equally permanent, and can be used in conjunction with all other durable pigments. The colour of burnt umber is warmer and richer than that of the raw product.

Cappagh brown, mineral brown, euchrome, is a highly manganiferous and ferruginous earth, obtained from the Cappagh mine, near Skibbereen, Ireland. When heated to 100° it loses water and assumes a fine reddish-brown hue, like that of burnt sienna. This pigment is suitable for work in oils or water-colour, and is permanent. Before grinding in oil, it should be dried at a temperature not exceeding 80°.

Caledonian brown possesses a reddish tint, altered upon ignition almost to black. This earth is composed chiefly of manganese and iron oxides and hydroxides; it is a useful and permanent colour, workable with all media. The original supplies are said to be exhausted, and a substitute is sold consisting of a mixture of Vandyke brown and burnt sienna (Church).

Manganese black, MnO_2, is the native manganese dioxide, very finely ground. It is expensive, too rapidly siccative, and without compensating advantages.

Pigments containing zinc. *Zinc white, Chinese white, snow white, flowers of zinc, Blanc de zinc, Zinkweiss,* zinc oxide, ZnO. This brilliantly white pigment (sometimes also called 'permanent white') is non-poisonous, permanent, innocuous to other pigments, and available for water-colour, tempera, fresco, and oils. In the last-named, however, it dries less satisfactorily than flake white, and with the lapse of time exhibits deficient opacity. For artists' work in water-colours, it cannot be excelled, and its use among painters generally, in enamels, mixed paints, dipping paints, combination white leads, and as a carrier for lake pigments, is rapidly extending. It is a mistake to consider that zinc white is wanting in covering or spreading power. In this respect it can hold its own very well against white lead, than which, however, it possesses somewhat less body.

Zinc carbonate, $ZnCO_3$, has been used as a pigment, but with little success: it is inferior in opacity and tint to zinc white.

Zinc sulphide, ZnS, is somewhat rarely used alone as a pigment, because, though possessed of considerable body, it usually fails with regard to purity of tint. Moreover, as an artists' colour it is inadmissible, from its tendency to injure certain other pigments. Associated with barytes, zinc oxide, magnesia, or the like, zinc sulphide enters into the composition of numerous white pigments now upon the market, such as Orr's white or lithopone, Griffith's white, &c.

Zinc-lead white is an intimate mixture of approximately 50 p.c. of zinc oxide with 50 p.c. of lead sulphate. The process of manufacture is similar to that of sublimed white lead. The colour resembles that of corroded white lead, and cannot be described as a pure white. This pigment is largely used in house paints and for the dipping paints in which agricultural implements and the like are painted by immersion and subsequent draining.

Lithophone, lithopone, zinc-baryta white, ponolith, Griffith's white, Orr's white, Charlton white, oleum white, patent zinc white. These and other names have been applied to a number of patented pigments, the basis of which is zinc sulphide. Associated with the zinc compound in most cases is barium sulphate, but calcium sulphate may also be used. Lithopone (the German name, which is now generally used) contains from 15 to 30 p.c. of zinc sulphide, according to the quality of the pigment: the best contains 30 p.c. From 7 to 10 p.c. of zinc oxide may be present, and the rest is barium sulphate. The parent of this class of pigments would seem to have been Orr's white enamel (1874). The lithopones are among the most important white pigments. These products are of good body, considerable covering power, and undeniable efficiency as substitutes for white lead, with which they compete in purity of tint. The lithopones are unaffected by atmospheres which darken lead paint. The darkening of lithopone is considered to be caused by the production of zinc by the action of light on zinc sulphide, which action may be prevented by forming an insoluble film around the zinc sulphide, thus preventing its reduction. A stable lithopone may be obtained by calcination of the zinc sulphide at 700°. The lithopones cannot be mixed with lead or copper pigments. They are everywhere extensively used in the oil-cloth industry.

(*Zinc chrome* and *zinc green* have been dealt with under *Chromium* and *Cobalt pigments* respectively.)

Zinc grey is a name applied to zinc dust (true zinc grey), and to various mixed pigments consisting of zinc oxide mingled with mineral black, lampblack, or the like.

Pigments containing barium. *Permanent white, constant white, barytes white, enamel white,* barium sulphate, $BaSO_4$, occurs in nature as the mineral barytes, the purer grades of which are pulverised, levigated, dried, and ground for the colourman's use. The variety of this pigment, known as *Blanc fixe, precipitated barytes,* or *artificial barytes,* is made artificially by precipitating a solution of barium chloride, or some other soluble salt of barium, with sulphuric acid or a soluble sulphate. The artificial product is somewhat purer than the natural pigment, but it is wanting in covering power and opacity generally to make it any use by itself. Although employed in water-colour painting, under the name of permanent white, it cannot be recommended as an oil colour. It is, however, one of the most absolutely permanent and inert pigments known. Barytes has been largely used as a 'filler' or 'extender' for white lead and other pigments.

Hamburg white, Dutch white, and *Venice white* are mixtures of barytes white and lead white.

Witherite, barium carbonate, $BaCO_3$, has very occasionally found its way into the market as a white pigment, but it mainly serves as the source from which barium chloride and other soluble barium salts are prepared.

(*Lithopone* has been described under *Zinc pigments,* and *Baryta yellow* under *Chromium pigments.*)

Pigment containing strontium. *Strontian white,* strontium sulphate, $SrSO_4$, has a very limited use as a white pigment. Its preparation from the mineral, celestine or celestite, is similar to that of permanent white from barytes. It is, perhaps, superior to barytes as a pigment, but is too costly for general use. (For *strontium yellow* v. chromium pigments.)

Pigments containing calcium. *Gypsum, Terra alba, satin white, mineral white, calcium sulphate,* $CaSO_4,2H_2O$, is obtained from the crude mineral by crushing, levigation, and drying. It is a permanent and useful pigment, innocuous to other colours, but possesses neither body nor opacity. Paper stainers and paper-makers use it in large quantities. The pigment known as satin white usually consists of a mixture of calcium sulphate and aluminium hydroxide, $Al_2O_3,3H_2O$. It possesses more body and covering power than gypsum alone.

Whitening, whiting, English white, Paris white, Spanish white, chalk, marble dust, Gilders' white, Kreide, Craie, calcium carbonate, $CaCO_3$. This pigment is used as a 'filler' or 'assistant' in mixed paints, but chiefly for whitewashing and in distemper work, as a painting-ground: it is permanent and can be mixed with all pigments, excepting vegetable colours, Prussian blue, emerald green, chrome yellow, and the like, which are likely to be affected adversely by alkalis. In oil, whitening is unserviceable and a bad drier.

Pigments containing magnesium. *Magnesium carbonate,* $MgCO_3$, prepared from the mineral magnesite by crushing and levigation, has sometimes been used as a pigment. It is permanent and available for admixture with other pigments, excepting such as are injured by alkalis.

Pigments containing silicon. *Pure silica,* SiO_2, ground to an impalpable powder, is useful for admixture with all pigments, excepting the silicious ochres, its principal function being that of a reinforcing or filling agent. Though inert and pre-eminently stable, it is too transparent for employment as a pigment alone. The main advantages of silica are its 'tooth' and its absolute permanency. *Steatite, Soapstone*

$$3MgO,4SiO_2,H_2O$$

is used to impart a glaze to some special paints.

(For *kaolin, v. Pigments containing aluminium.*)

Pigments containing, or consisting chiefly of, carbon. *Soot black, vegetable black, lampblack, smoke black, candle black, flame black, gas black, carbon black.* These widely used pigments are soots, obtained by the incomplete combustion of mineral oils, greases, and fat-oils, resins, tarry matters, and natural gas. Carbon or gas black is mostly produced in the combustion of the last-named. *Acetylene black* is an especial variety of gas black, obtained by exploding together in a cylinder acetylene gas and a limited supply of oxygen. Flame black is derived from tar, naphthalene, pitch, &c.: true lampblack is mainly from liquid raw materials. These pigments are nearly pure carbon, perfectly inert, entirely permanent, and uninjurious to all other colouring matters, with the exception of a few unstable organic compounds, liable to be decolorised by carbon. A very fine, pure lampblack is the pigmentary basis of Chinese or Indian ink.

Animal black, bone black (*Beinschwarz*), *ivory black, Paris black, sugar house black.* The first is obtained as the carbonaceous *residuum* of the destructive distillation of miscellaneous animal offal, the second in a like manner from bones, and the third is or should be produced similarly from waste ivory, but it is generally prepared from the spent animal charcoal used by sugar refiners. Ivory black—particularly when the lime salts have been removed by digestion in hydrochloric acid—is the most intense of the black pigments: it is stated (Toch) that lampblack will make a light mark on ivory black. The animal blacks exert considerable decolorising power when associated in an aqueous medium with organic colouring matters: hence they are more advisedly used in oils than for water-colour painting. Notably hygroscopic, such pigments should be dried before being ground in oil. *Soap black* is a form of ivory black moulded into pastilles with a little gum-water.

Charcoal black, Frankfort black, German black, drop-black, blue-black, vine-black, and the like, may shortly be described as charcoals. They are made by calcining in closed vessels materials of the most diverse descriptions, and, as may be expected, vary greatly in value, quality, and cost. The finest bluish-black and velvety products are obtained from vine and beech twigs, fruit stones, coco-nut shell, grape husks, and dried wine-lees. Inferior charcoal blacks result from the charring of very many non-resinous, soft woods. Bass, willow, and maple woods, also paper mills' refuse, are among the materials employed. Drop-black is so named, because it is sent into the market in the form of pear-shaped drops, into which it has been moulded with the aid of a little glue-water.

Mineral black, slate black, oil black, or *black chalk* is a brownish-black to blue-black, highly carbonaceous shale, occurring in Bavaria, Spain, Italy and elsewhere, suitable for pigmental use, after crushing and levigation or wet-grinding.

Coal blacks are somewhat similar. In common with other carbon-pigments, mineral black dries slowly, but is possessed of great permanency. The more intense blacks, of artificial origin, are superseding the different varieties of shale- and coal-blacks.

Graphite, plumbago, or *black lead* is a dark grey to black pigment, of absolute permanence, available for use with all media, and miscible with other pigments. Nearly pure carbon, and extraordinarily inert, it is a valuable ingredient of paints used as protective coatings for metals. This application of plumbago is exemplified in the familiar stove polishes. With white pigments, graphite supplies the artist with neutral greys. Its use in the manufacture of drawing pencils need merely be mentioned here.

Prussiate black is the washed and dried carbonaceous residue, obtained as a bye-product in the manufacture of potassium ferrocyanide.

Prussian black results from the calcination of Prussian blue, is a mixture of carbon and oxide of iron, possesses a brownish shade and presents no particular advantages as a pigment.

Bistre is a brownish-black, bituminous soot, obtained chiefly from the smoke of beechwood. It is purified for use by digestion and repeated washing with boiling water, levigation, and grinding with gum-water or glucerol, or both. Bistre, which is not used in oils, is somewhat fugitive.

Bone brown is prepared by calcining bones until they are of a brownish colour, and grinding the product.

Vandyke brown, as generally met with in this country, is a highly bituminous, ferruginous earth. Though of a fine, rich hue, this variety of Vandyke brown is decidedly fugitive, especially in water-colour. Two other, more permanent, but far less richly-tinted pigments, sold under the same name, consist of a brown variety of *caput mortuum,* and a calcined ferruginous ochre, respectively. Imitation Vandyke browns are made, consisting of ochre, colcothar, and lampblack, in admixture.

Cassel brown, Rubens' brown, Cologne earth, Cullen earth, coal brown, and the like are, for the most part, varieties of brown coal or lignite. Some are ochreous in character and approximate in composition to the umbers. These pigments are subject to such variability of composition that they cannot safely be trusted for artistic purposes.

Asphaltum, bitumen, mineral pitch, mummy. The use of asphalt or native bitumen, as a pigment, has been virtually abandoned by artists, but large quantities from Trinidad and elsewhere are consumed in the manufacture of varnishes, such as Brunswick black, carriage varnish, and black japan. Extreme brittleness is a disadvantageous feature of asphalt coatings. The use of native bitumen by the ancient Egyptians, for embalming the dead, led to the application, in after-centuries, of the exhumed remains, ground to dust (bitumen, bones and all), as an artists' pigment, under the name of *mummy.* This colour, in an oil vehicle, is more permanent than asphaltum.

Other pigments of organic origin. *Indian yellow, Purree, Piuri, Purrea Arabica,* is composed mainly of the impure, basic magnesium salt of euxanthic acid

$$(OH{\cdot}C_6H_3{<}^{O}_{CO}{>}C_6H_3{\cdot}O\,CH(OH){\cdot}[CH{\cdot}OH]_4{\cdot}COOH,2H_2O)$$

The compound is $Mg{\cdot}C_{19}H_{16}O_{11},5H_2O$, and is excreted in the urine of cows fed upon the leaves of the mango tree, *Mangifera indica* (Linn.). This pigment is exclusively made by natives of India at Monghyr, Bengal. The urine is evaporated, the yellow residue dried, collected on calico and rolled into balls, which are sold in the native bazaars. Indian yellow is moderately permanent in oils, well suited for fresco work, somewhat fugitive in water-colour, and apt to injure certain of the lakes when associated with them. It is unaffected by sulphur compounds.

Gallstone, a yellow pigment derived from a calculus formed in the gall-bladder of oxen. It has been used as a water-colour, but is of no permanence and little value.

Gamboge, gutti, gummigutt, gomme-gutte. This familiar pigment is a gum-resin yielded by Malayan, Siamese, Burmese, Indian, and Cingalese species of *Garcinia.* Gambogic or cambogic acid, the principal of the resin acids constituting the pigment, is $C_{30}H_{35}O_6$ (Buchner). Gamboge is better adapted as an oil pigment than for water-colours, but even in oil it is not permanent unless beeswax, solid paraffin, or a resin such as Venice turpentine or copal be present also. As a water colour, gamboge is best avoided: alkalis darken it, and light not infrequently diminishes its brilliancy of tint. If admixed with cadmium sulphide or barium chromate, it is less alterable, but aureolin and purree are more trustworthy pigments.

Dragon's blood. The dragon-tree of the Canary Islands, *Dracœna Draco* (Linn.), the rattan tree, *Calamus draco,* and a variety of other plants, yield deep red-coloured resins known in commerce under the above name, *v.* RESINS. As a pigment it is fugitive and untrustworthy. It dries poorly and is injured by certain other pigments, such as flake white.

Hooker's green and *Prussian green* are 'mixed' pigments, composed of gamboge and Prussian blue.

Indigo, indigotin, indigo blue, $C_{16}H_{10}N_2O_2$ or $C_6H_4{<}^{CO}_{NH}{>}C:C{<}^{CO}_{NH}{>}C_6H_4$, is formed by the fermentation of the glucoside, indican, $C_{52}H_{62}N_2O_{34}$, a constituent of various species of *indigofera,* especially *I. tinctoria* (Linn.), and of other plants, such as woad, *Isatis tinctoria* (Linn.). Commercial indigo is impure indigotin and is greatly improved in quality and hue ('intense blue') by successive treatment with hydrochloric acid, hot water, sodium hydroxide solution and strong alcohol (Church). Synthetic indigo is now a formidable rival to the natural product, and is stated to contain 97 p.c. of the pure pigment. Indigo in oils and water is wanting in permanency, and suffers deterioration in the presence of chromes and other pigments.

Sepia is the dark brownish-black pigmentary matter contained in the ink-bags of the *sepia,* or cuttlefish, and allied cephalopodous organisms. The method of preparation consists in boiling the crude sepia with caustic soda solution, filtering, precipitating the colouring matter from the alkaline solution by the addition of hydrochloric acid, collecting, washing, and drying. Sepia is permanent, inert, and suitable both for oils and aqueous media. It is especially useful for monochrome work and in water-colour painting. The exact chemical nature of the compound

melanin (apparently a weak organic acid, *sepiac acid*), which constitutes 78 p.c. of the pigment, is at present incompletely studied.

Pigments composed of lakes. The lake colours have, during the past two decades, become of prominent importance. They are fully dealt with in the article 'LAKES,' vol. iv. p. 29. In contradistinction to the pigments already described, which, for the most part, are *substantive* colours, *i.e.* consist of homogeneous particles (*e.g.* aureolin, chrome green, lamp-black), the lake pigments are *adjective* products, and are compounds of a soluble (usually) organic colouring principle with an insoluble inorganic base, most often non-pigmental, and generally, but not invariably, white. Among the bases employed are aluminium hydroxide, barium sulphate, calcium sulphate, zinc oxide, kieselguhr, green earth, kaolin, and iron oxide, but many others are used. Three classes of lakes come within the category of pigments: (1) lakes made from animal colouring matters; (2) lakes prepared from vegetable substances; and (3) lakes obtained from coal-tar products. Lakes belonging to the first two classes were in use at a very early period, but the far more numerous lakes made from artificial colouring principles are of quite modern introduction.

Carmine is the most important example of a lake pigment belonging to the first of these classes. The dried females of the cochineal insect, *Coccus cacti*, are boiled with water, alum, stannous chloride and sodium carbonate being added. After standing for a few days, the decanted liquid throws down the pigment as a crimson precipitate, which is washed and dried, *v.* LAKES.

Cochineal pigments, though beautiful in hue, are excessively fugitive, and should be excluded from the artist's palette.

Lac lake, Indian lake, lac dye lake, lack lack. A resin called gum lac is formed on *Ficus religiosa* (Linn.) and other trees, when punctured by *Tachardia lacca*, an organism similar to the cochineal insect. The exudation, though initially vegetable, runs from the female insect and solidifies on the twigs as stick lac. This, extracted with water, yields lac dye, and the insoluble residue constitutes the seed lac and shellac of commerce. After purification, the lac dye (laccaic acid, $C_{16}H_{12}O_8$, Schmidt) is extracted with an alkaline solution and subsequently treated with alum. The precipitated lac lake is washed and dried. This pigment is less fugitive than the cochineal lakes, but its hue is inferior and it is seldom used (*v.* LAC DYE).

Among the lake pigments belonging to the second class mentioned above, those prepared from vegetable substances are the natural *madder lakes.* The madder root, *Rubia tinctorum* (Linn.), contains, together with purpurin, $C_{14}H_5O_2(OH)_2$, the glucoside ruberythric acid, $C_{26}H_{28}O_{14}$, which by hydrolysis yields dihydroxy-anthraquinone or alizarin

$$C_{14}H_6O_2(OH)_2$$

This compound is capable of giving, according to the nature and proportions of the bases employed in association with the acidified and washed madder root (alumina, lime-alumina, iron oxide, copper oxide, *et alia*), crimson, pink, purple, brown, and plum-coloured lakes. Under similar conditions, purpurin gives orange-hued and bright-red products. Whether natural or of artificial origin, the madder pigments, although alterable by prolonged exposure, are, as a class, far less perishable than the coccus lakes. This statement does not apply to the so-called 'yellow madder,' yellow lake and the like, which are extremely fugitive pigments, *v.* LAKES.

There remain to be considered the lakes obtained from coal-tar products. These, to a great extent, have superseded the lakes of animal and vegetable origin. They have already been described in the article 'LAKES,' to which reference may be made.

Unfortunately, the pigments obtained from the artificial colouring matters, with the exception of the alizarin lakes and some of the pigments produced from the azo colours, are neither light-fast nor are they damp-fast or air-fast. Many of the most brilliant products are deteriorated by a few hours' exposure. Nevertheless a considerable number of permanent artificial lakes are now available, *e.g.* para-nitraniline lakes, metanitroparatoluidine lakes, Litho red lakes, and the Helio fast reds of Bayer.

As the result of the examination of 63 coal-tar colours used as pigments, Krais (Zeitsch. angew. Chem., 1912, 25, 2193) found that 40 could be classed as good, 11 of them being practically as fast as good mineral colours such as Victoria green, Chrome yellow, &c. These were Helio chrome yellow GL, Algol Red 5G, Helio Fast Red RL, Algol Blue 3R, Lithol Fast Orange R, Indanthrene Blue GGSZ and RZ, and Permanent Red 2G extra, 6B. A yellowish-scarlet lake of great beauty and fastness to light has been obtained from a monoazo dyestuff derived from *m*-xylidene sulphonic acid and R. salt (Eng. Pat., 164053, 1921).

Stability. For many years past much attention has been devoted to the subject of the permanency or stability of pigments under various conditions. The agencies to which the painter's colours may ordinarily be subjected are light, air (possibly in association with varying quantities of noxious gases, such as hydrogen sulphide and sulphur dioxide), moisture, the vehicle or medium used, the associated pigments, and, in some cases, the painting ground.

As long ago as 1772, Sir Joshua Reynolds tested some of the pigments he used, and since his time many observers have similarly experimented, but in a more systematic and scientific manner: among them, Dyckman, Andrew, Decaux, Simpson, Rood, Hartley, Russell and Abney, Church and Laurie, *v.* PAINTS. Much good work in this connection has been done by the Deutsche Gesellschaft für Beförderung rationeller Malverfahren; and during the years 1894–1904, the Burlington Fine Arts Club carried out a series of valuable tests of water-colour paints, exposed to light under different conditions. Ogden N. Rood, whose experiments were made with washes of several dozen water-colours upon drawing-paper during three and a half summer months' exposure, found only the following twelve pigments unaffected: yellow ochre, Roman ochre, cadmium yellow, Indian red, light red, *jaune de Mars*, cobalt, smalt, French blue, burnt sienna, burnt umber, and

terre verte. The experiments of Russell and Abney, upon the action of light on water-colours, showed that when washes upon Whatman paper were exposed for nearly two years to light and air, the following pigments remained unchanged: Indian red, Venetian red, burnt sienna, chrome yellow, lemon yellow, raw sienna, terre verte, chromium oxide, Prussian blue, cobalt blue, French blue and ultramarine ash. In the table below, the approximate order of instability of the pigments, the most fugitive being placed first, is set forth :—

1.*Carmine	16.*Violet carmine	28. Indian red
2.*Crimson lake	17.*Purple carmine	29. Venetian red
3.*Purple madder	18.*Sepia	30. Burnt sienna
4.*Scarlet lake	19. Aureolin	31. Chrome yellow
5.*Payne's grey	20. Rose madder	32. Lemon yellow
6.*Naples yellow	21. Permanent blue	33. Raw sienna
7.*Olive green	22. Antwerp blue	34. Terre verte
8.*Indigo	23. Madder lake	35. Chromium oxide
9.*Brown madder	24. Vermilion	36. Prussian blue
10.*Gamboge	25. Emerald green	37. Cobalt blue
11.*Vandyke brown	26. Burnt umber	38. French blue
12.*Brown pink	27. Yellow ochre	39. Ultramarine ash
13.*Indian yellow		
14. Cadmium yellow		
15. Leitch's blue		

The colours marked with an asterisk altered during only four months' exposure; Nos. 27 to 39 showed no change during two years. Of thirty-four mixtures, only three remained unaltered at the end of the period; but six mixtures containing Prussian blue, though changed at first, returned more or less to their original colour when kept in the dark for six weeks. Prussian blue, which has suffered in tint from exposure to sunlight, is well known to possess the remarkable property of recovering its colour when placed in darkness. Among Russell and Abney's conclusions were: (1) that mineral colours are far more stable than vegetable pigments; (2) that moisture and oxygen are essential for changes to be effected in vegetable colours; (3) that in a mixture of colours having no direct chemical action on one another, light causes the unstable colour to fade, leaving the stable pigment virtually unaltered; and (4) that the more refrangible rays of light, which produce the greatest change in pigments, are present in comparatively small proportion in the lights usually employed in illuminating a room or picture-gallery.

Abney has also shown that the use of a slow current of ozone in a few hours gave nearly the same results as those obtained by months of exposure to ordinary daylight, but moisture, not hydrogen peroxide, must be present (J. Roy. Soc. Arts, 63, 95).

The German society above-mentioned selected the following list of *normal colours* for oil-painting, as having been shown by experience to be the most permanent and trustworthy under the influences of light and air: white lead, zinc white, Naples yellow, cadmium yellow (darker shades), Indian yellow, brown and yellow ochre, terra di siena, burnt ochre, red ferric oxide colours, vermilion, madder (alizarin) lake, cobalt blue and green, ultramarine, the Prussian blues, chromium oxide green, green earth, umber, asphalt, mummy, ivory black and lampblack (Zerr and Rübencamp).

The Burlington Fine Arts Club trials, which were made with washes of a considerable number of moist water-colours upon Whatman paper exposed to dry air, moist air, and in glazed frames, respectively, were totally unfavourable to gamboge, Indian yellow, Vandyke brown, crimson lake and vermilion; but it was proved that Prussian blue, indigo, sepia and other pigments liable to change in damp air, may be regarded as tolerably stable if so framed as to be kept dry.

For water-colour and tempera painting, flake white, pale cadmium, true Naples yellow, chrome yellow, artificial vermilion, malachite green, madder brown, bistre, and sepia, must be added to this last list as being quite untrustworthy. Other pigments, in addition to the foregoing, are unsuitable for fresco work and stereochromy, *e.g.* the Prussian blues, Antwerp blue, all the chromates and the madder colours.

The pigments regarded by Decaux as quite unchangeable in oils are: zinc white, flake white, yellow ochre, Naples yellow, deep cadmium, raw sienna, red ochre, Mars red, Venetian red, burnt Italian earth, green oxide of chromium, terre verte, green ultramarine, artificial ultramarine, cobalt blue, and ivory black.

Eibner has studied the catalytic action of zinc white in accelerating the bleaching action of light upon organic dyestuffs, lakes and mineral pigments used by artists. The bleaching was found to be greatest when the painted surfaces were exposed under glass and when a binding agent containing water or glycerin was used; with oil media the action is much less. With the pigments experimented on, the bleaching action was greatest in the case of chrome yellow, zinc and cadmium yellow, and vermilion, slight in the case of ultramarine, Guignet's green and cobalt violet, whilst cobalt blue and green and the earth colours were unaltered. Zinc carbonate, silicate and sulphide exert a similar but reduced action, whilst precipitated and native barium sulphate, chalk, white lead and lithopone are without any such influence on the action of light (J. Soc. Chem. Ind., 1911, 1170).

With reference to the action of foul gases, it may be stated generally that the lead and copper pigments are especially sensitive to hydrogen sulphide; the chromates of zinc and barium are liable to turn green in the presence of sulphur dioxide; ammoniacal vapours will injuriously affect the copper greens and Prussian blues; acid fumes may injure ultramarine, and reducing or oxidising gases attack indigo.

Certain pigments should not be used in conjunction: thus, aureolin and indigo, aureolin and cochineal lakes, cadmium yellow and emerald green, vermilion and malachite, white lead and lithopone, and chrome yellow and lithopone, are examples of mixtures, the components of which may mutually react when intimately mixed. In an oil medium, there is less likelihood of such injurious interaction than with water-colour pigments, but it may be affirmed that it is in general wiser to mix pigments on the palette than to grind them together. E. G. C.

PILBARITE *v.* GUMMITE.

PILCHARD OIL. A pale yellowish-brown oil, obtained by pressing the pilchard (*Clupea pilchardus*). Caught off the coasts of Cornwall

from July to November. Gives the following numbers on analysis :—

Free fatty acids (asoleic acid)	8·15–9·32 p.c.
Saponification value	186·0–189·6
Reichert-Meissl value	0·45–0·55
Insol. fatty acids and unsapon. matter	93·5–93·2
Unsaponifiable matter	0·95–1·02
Sp.gr. at 15·5°/15·5°	0·9328–0·9313
Iodine value (Wijs)	170·4–172·7
Refractive index (D line) at 40°	1·47510–1·47425
Viscosity (seconds Redwood) at 40°	121·0–115·0

Insoluble fatty acids and unsaponifiable matter :

Neutralisation value	193·7–187·2
Mean molecular weight	289·5–292·8
Iodine value (Wijs)	178·2–180·3
Oxidised fatty acids	trace
Ether-insoluble bromides	55·8 p.c.–56·2 p.c.
Melting-point	34·8°
Titre	28·2°

The oil does not form an elaïdin, but reacts readily with sulphur chloride. The ether insoluble bromides (prepared from the fatty acids by the method of Eibner and Muggenthaler (Farber-Zeit. 1912, 18, 131)) are probably the octobromides of clupanodic acid, $C_{17}H_{27}COOH$. The oil darkens in colour on exposure to light and air and deposits oxidised fatty acids, which renders it unsuitable as a lubricant or as a substitute for linseed oil. It is mainly used for the manufacture of soft soap. The yield from a given weight of the fish varies from 1½ gallons per 100 kg. of pilchards to 2 or 2½ gallons. The total production of pilchard oil during the last five years was approximately as follows: 1917, 9500 galls.; 1918, 1500 galls.; 1919, 60,000 galls.; 1920, 44,000 galls.; 1921, 60,000 galls. (Langton, Trans. Soc. Chem. Ind. 42, 1923, 47 T.).

PILLIGANINE *v.* LYCOPODINE.

PILOCARPIDINE, PILOCARPINE, *iso*-PILOCARPINE *v.* JABORANDI.

PILOLITE. Hydrated aluminium and magnesium silicate, approximating in composition to $4MgO{\cdot}Al_2O_3{\cdot}10SiO_2{\cdot}15H_2O$, forming tough felted masscs of fine fibres, and consequently named from πῖλος, felt. The material is very light and porous (sp.gr. in the mass 0·68–1·34), cream-yellow to buff in colour, dull and opaque, and quite soft (H. = 1). It absorbs water like a sponge; and when immersed in water swells considerably and becomes soft and viscous, but does not disintegrate. When calcined it shrinks enormously, becoming hard and brittle, though still light and porous. Before the blowpipe it fuses to a somewhat blebby colourless glass. Hydrochloric acid attacks it only slightly. Most of the minerals popularly referred to as *Mountain-leather* (*Cuir de montagne*, Ger. *Bergleder*), *Mountain-cork* (*Liège de montagne*), *Mountain-wood*, *Mountain-paper* (*Carton de montagne*), &c., belong to this species. Such a structure might, of course, be taken on by some other minerals, *e.g.* by matted fibres of amphibole-asbestos. Conversely, pilolite can be included under the general term asbestos (*q.v.*), and it can be used for some of the same technical purposes.

A. Fersmann (Bull. Acad. Sci. St.-Pétersbourg, 1908) includes pilolite, togcther with similar minerals described under the names palygorskite, lassallite, hydrous anthophyllite, &c., in his *palygorskite group*. The composition is explained by the mixing of two molecules, $A = H_8Mg_2Si_3O_{12}$ (called parasepiolite, *i.e.* sepiolite or meerschaum (*q.v.*) with the addition of $2H_2O$), and $B = H_{12}Al_2Si_4O_{17}$ (paramontmorillonite, *v.* montmorillonite), viz.—

α-palygorskite	$A_1B_2 = H_{32}Mg_2Al_4Si_{11}O_{46}$
β-palygorskite	$A_1B_1 = H_{20}Mg_2Al_2Si_7O_{29}$
α-pilolite	$A_2B_1 = H_{28}Mg_4Al_2Si_{10}O_{41}$
β-pilolite	$A_3B_1 = H_{36}Mg_6Al_2Si_{13}O_{53}$

Mineral substances of this kind are of wide distribution, and are usually found in mineral veins and rock crevices, where they have been formed by circulating watcrs. Pilolite, for example, has been found at numerous localities in Scotland in rocks of all kinds—andesite, basalt, granite, serpentine, gneiss, sandstone, conglomerate, and shale. A particularly fine quality of material, forming thin flexible white sheets very like glove kid, appears to be of abundant occurrence in the prefecture of Sui-fu, prov. Süchwan, China. Analysis of this material gave the formula $2MgO{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}7H_2O$. L. J. S.

PILOPIC ACID *v.* JABORANDI.

PILOSINE *v.* JABORANDI.

PIMARIC ACID *v.* RESINS.

PIMELIC ACID $C_7H_{12}O_4$. Twenty-five isomeric acids having this formula have been prepared, and of these three are known as *pimelic acid*.

Normal pimelic acid $CO_2H[CH_2]_5CO_2H$, obtained by the oxidation of fats (Bouveault, Bull. Soc. chim. 1898 [iii.] 19, 562), and of castor oil (Gantter and Hell, Ber. 1884, 2213); prepared by the oxidation of suberone (*v.* suberic acid) with nitric acid (Schorlemmer and Dale, Annalen, 199, 147); by heating pentanetetracarboxylic acid at 200°–220° (Perkin and Prentice, Chem. Soc. Trans. 1891, 825); by treating αε-dichloro-, dibromo-, or di-iodopentane with potassium cyanide and hydrolysing the nitrile thus formed (Braun, Ber. 1904, 3588; Hamonet, Compt. rend. 1904, 139, 59); by the interaction of the sodium compound of ethylcyanacetate and trimethylene dibromide (Carpenter and Perkin, Chem. Soc. Trans. 1899, 924); by the interaction of piperidine, cyanogen bromide, and phosphorus pentachloride (Braun, Chem. Zentr. 1909, ii. 1993); by the action of sodium in amyl alcohol on salicylic acid (Einhorn and Willstätter, Ber. 1894, 33; Einhorn and Lumsden, Annalen, 286, 260; Walker and Lumsden, Chem. Soc. Trans. 1901, 1198); by the reduction of furonic acid with hydriodic acid and red phosphorus (Baeyer, Ber. 1877, 1358); by the reduction of piperylene dicarboxylic acid with sodium in alkaline solution (Willstätter, Ber. 1898, 1550); by the interaction of trimethylene bromide and malonic ester and heating the product thus formed (Perkin, *ibid.* 1884, 3289). Crystallises in needles from benzene and in plates from watcr; m.p. 105°. By heating the acid with lime, *cyclo*hexanone is produced. Substituted alkyl pimelic acids are produced by the reduction of substituted *o*-phenol carboxylic acids (Einhorn, Annalen, 295, 173; Chem. Zentr. 1897, i. 1006; D. R. P. 90556).

For nitrogenous derivatives, *see* Schmidt (Arch. Pharm. 1915, 253, 604).

β-pimelic acid is identical with *normal pimelic acid*.

Pimelic acid, iso-*Propylsuccinic acid*—

$$(CH_3)_2CH{\cdot}CH(CO_2H){\cdot}CH_2CO_2H$$

prepared by fusing *d*-camphoric acid with caustic alkali (Hlasiwetz and Grabowski, Annalen, 145, 207; Mahla and Tiemann, Ber. 1895, 2152; Crossley and Perkin, Chem. Soc. Trans. 1898, 22); by the action of nitric acid on β-*iso*propyl-δ-ketohexoic acid (Crosslcy, Chem. Soc. Trans.

1902, 676); by the action of potassium permanganate on tetrahydrocarvone in alkaline solution (Baeyer and Oehler, Ber. 1896, 36); by treating amylene bromide with potassium cyanide and hydrolysing the resulting nitrile (Auwers and Mayer, Annalen, 298, 150, 177); by similarly treating *iso*caprolactone (Blaise, Compt. rend. 124, 90); by the reduction of teraconic acid, dimethyl-4-citraconic acid, or -mesaconic acid with sodium amalgam (Fittig and Krafft, Annalen, 304, 206); by treating *iso*thujone with potassium permanganate and sodium hypobromite (Wallach, Ber. 1897, 423). M.p. 116°–117° (Bentley, Perkin, and Thorpe, Chem. Soc. Trans. 1896, 274); readily soluble in chloroform, benzene, and warm water. Oxidation with potassium dichromate and sulphuric acid converts it into terebic acid, $C_6H_{10}O_4$ (Lawrence, Chem. Soc. Trans. 1899, 527).

γ-Pimelic acid, β-methyladipic acid—

$$CO_2H{\cdot}CH_2CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CO_2H$$

This acid contains an asymmetric carbon atom, and hence exists in two stereoisomeric forms.

d-Acid, prepared by the oxidation of citronellal or citronellic acid (Tiemann and Schmidt, Ber. 1896, 908; Semmler, *ibid.* 1890, 2257), of *iso*pulegol (T. and S., *ibid.* 1897, 25), of pulegone (Semmler, *ibid.* 1892, 3516), or of menthone (Manasse and Rupe, *ibid.* 1894, 908). Can be obtained from menthol (Beckmann and Mehrländer, Annalen, 289, 378). Melts at 93°–94·5° (Wagner, Ber. 1894, 1642), at 84·5° (Semmler, *l.c.*).

l-Acid, prepared by the oxidation of *l*-citronellal (T. & S. Ber. 1896, 923), m.p. 84·5°

Inactive acid. Prepared by the oxidation of *i*-citronellal (T. & S. *ibid.* 1896, 925) or from equal quantities of the *d*- and *l*- acids: m.p. 93°–94°.

iso*Pimelic acid, αα-methylethylsuccinic acid*

$$\begin{array}{l} CH_3{\cdot}C(C_2H_5)CO_2H \\ \quad\quad\quad\quad | \\ \quad\quad\quad CH_2{\cdot}CO_2H \end{array}$$

prepared from amylene bromide and potassium cyanide (Hell, Ber. 1891, 1390; Bauer and Schuler, J. 1878, 733), or from the mixture of tricarboxylic acid esters (b.p. 135°–160° at 0·15 mm.), obtained by treating ethyl α-bromomethylethyl acetate with sodiomalonic ester in xylene solution (Auwers and Fritzweiler, Annalen, 298, 166; 292, 154, 182); m.p. 103°–104°.

PIMENTA *v.* LAURUS NOBILIS.

PIMENTHOL *v.* CAMPHORS.

PINAKOL. A photographic pyrogallol developer containing sodium aminoacetate in place of part of the alkali usually present.

PIMENTO. Pimento or Allspice is the dried, full-grown but unripe fruit of *Pimenta officinalis* (Lindl.).

The plant is indigenous to the West Indies and is largely cultivated in Jamaica, whence our supplies are derived. The globular berries, dark purple when fresh, brown when dry, are from 5 to 8 mm. in diameter. They are enclosed in a two- but sometimes one- or three-celled fruit. They are gathered when of full size but still not quite ripe, and dried in the sun.

The characteristic flavour is due to an aromatic, pungent, volatile oil, resembling in smell that of cloves; other important constituents are a fixed oil, tannin, resin, and much starch. Full analyses by Richardson (U.S. Dept. of Agric., Div. of Chem. Bull. 13, 221) yielded the following results:—

	Whole	Ground	
		Max.	Min.
Water	6·19	8·82	5·51
Ash	4·01	5·53	3·45
Volatile oil	5·15	3·02	2·07
Fixed oil	6·15	6·92	3·77
Fibre	14·80	18·98	10·45
Proteid	4·38	5·42	4·03
Nitrogen	0·70	0·87	0·64
Quercitannic acid ('tannin equivalent')	10·97	12·74	8·27

Uses.—Pimento finds its chief use as a condiment, but it was formerly *officinal* in the British Pharmacopœia together with an *aqua* and the essential oil.

Adulteration.—Comparatively little is sold in the ground state in this country, so that pimento is rarely if ever adulterated here. Very few samples, however, are examined under the Sale of Food and Drugs Acts. The usual spice adulterants may be looked for, namely, added starches, ground olive stones, and the shells of cocoanut and almond, &c.

Analysis.—Microscopical examination will suffice to detect all the likely adulterants of vegetable origin. The most characteristic structures to be observed are minute starch grains, usually about 8μ in diameter and not exceeding 12μ, with a distinct hilum, often joined in pairs or triplets, or larger aggregates; numerous colourless stone cells, some very large; and pigment cells containing irregular port wine or amber-coloured masses of resin or gum.

The most useful determinations are ash, tannin, and fixed ether extract. Unless adulteration is discovered by the microscope, anything further is seldom required. Should olive stones or nutmeg be suspected of being present, their special characters are given under PEPPER (*q.v.*).

The direct determination of tannin is neither easy nor satisfactory, but very fair results may be obtained by calculating the quercitannic acid from the proportion of oxygen absorbed from potassium permanganate.

The process, due to Richardson (U.S. Dept. of Agric., Div. of Chem. 13, 167), is as follows: Boil 2 grms. of the sample, after thoroughly extracting with ether, with 300 c.c. of water for 2 hours, cool, make up to 500 c.c. with water and filter. Mix 25 c.c. of the filtrate with 750 c.c. of water, add 25 c.c. of indigo solution (made by dissolving 6 grms. of potassium sulphindigotate in hot water, cooling, adding 50 c.c. of sulphuric acid (conc.) and making up to 1 litre). Then titrate with the permanganate solution (1·333 grms. per litre) until the liquid becomes of a bright yellow colour. Note the number of c.c. used. Ascertain the equivalent of the permanganate in terms of N/10 oxalic acid and calculate the number of c.c. of the former used in oxidising the pimento solution. Convert this into its equivalent number of c.c. of oxalic acid. Each c.c. of the oxalic acid =0·0623 grm. of quercitannic acid.

The following table will afford some idea of the figures yielded by genuine samples, but comparatively few analyses of authentic specimens are on record.

Analyses by Winton, Ogden and Mitchell

Ann. Rep. Connect. Agricult. Station, 1898, p. 204.

	Max.	Min.	Average
Moisture	10·14	9·45	9·78
Ash	4·76	4·15	4·47
,, soluble in water	2·69	2·29	2·47
,, insol. HCl	0·06	0·00	0·03
Ether extract, volatile	5·21	3·38	4·05
,, ,, fixed	7·72	4·35	5·84
Alcohol extract	14·27	7·39	11·79
Starch (diastase method)	3·76	1·82	3·04
Fibre	23·98	20·46	22·39
N	1·02	0·83	0·92
Quercitannic acid	12·48	8·06	9·71

Standards.—The United States standard for Allspice provides that the quercitannic acid shall not be less than 8 p.c., the ash not more than 6 p.c., the ash insoluble in HCl not more than 0·5 p.c. and the fibre (which should be determined as in pepper) (*q.v.*) not more than 25 p.c. C. H. C.

PIMENTO OIL *v.* Oils, Essential.

PINABIETIC ACID, $C_{20}H_{30}O_2$. A crystalline resin acid, found in the less volatile fractions obtained on steam-distillation of pine oil. The corresponding chloride *pinabietyl chloride* yields carbon monoxide and hydrogen when distilled under reduced pressure, together with a hydrocarbon *pinabietene*, $C_{19}H_{28}$ (octahydromethylretene.) (Aschan, Annalen, 1921, 424, 117, 150).

PINACHROMY and **PINATYPE.** Processes of colour photography devised by E. Koenig (*v.* J. Soc. Chem. Ind. 1906, 657).

PINACONES and **PINACONE TRANSFORMATION** *v.* Ketones.

PINAVERDOL (1 : 1′ : 6′-trimethyl*iso*cyanine iodide). Used as a sensitising dye for photographic plates. Monoclinic crystals: $a : b : c = 1·1014 : 1 : 1·6053$. $\beta = 88° 20'$, varying from prismatic to tabular. Show brilliant reflection pleochrism with metallic colours. Crystals less than 0·02 mm. in thickness transmit light, and show strong absorption and pleochroism. Refractive indices, α about 1·58, β and γ more than 1·75, probably near 2·0; optically negative (Wherry and Adams, J. Washington Acad. Sci. 1919, 9, 396).

PINCHBECK. An alloy of zinc and copper brought into notice by Christopher Pinchbeck in the latter part of last century. It was formerly much employed in the making of watch-cases, and other small ornamental articles in imitation of gold. Its composition is variable, but usually consists of 9 parts of copper to 1 part zinc.

PINE-APPLE. The fruit of *Ananas sativus* (Schult.) [*Bromelia ananas*] a tropical plant, grown largely in the West Indies, the Azores, Singapore, Florida, the Bahamas, Natal, and other hot countries. According to Munson and Tolman (J. Amer. Chem. Soc. 1903, 25, [iii.] 272), the average composition (38 samples) of fresh pine-apples, 21 from Florida, 10 from Cuba, 4 from Porto Rico, 2 from the Bahamas, and 1 from Jamaica, is

Water	Protein	Free acid (as H_2SO_4)	Reducing sugar	Cane sugar	Ash	Insoluble matter
85·83	0·42	0·60	3·91	7·59	0·40	1·52

In different specimens, the reducing sugars varied from 1·76 to 9·75 p.c.; the cane sugar from 3·0 to 10·5 p.c. According to Lindet (Bull. Soc. chim. 1884, 40, 65), pine-apples contain 1 p.c. or more of mannitol. Pine-apple juice is said to contain an enzyme, *bromelin*, which resembles pepsin and can digest a thousand times its weight of proteids in a few hours. It can be precipitated from the juice by the addition of common salt, and can operate in acid, neutral or alkaline media (J. Franklin Inst. 1902, 154, [iv.] 262). The leaves of the plant furnish a fibre which can be used for the manufacture of rope, being stronger than flax. It is also used in the Philippines for the preparation of a cloth (Board of Trade Journal, Dec. 1898, 671; also Bull. Imp. Inst. 1904, 2, 168). Pine-apples are often canned, being preserved in their own saccharine juice, with or without the addition of sugar. Analyses of commercial samples by Munson and Tolman (*l.c.*) gave the following average figures:—

	Water	Protein	Free acid	Reducing sugar	Cane sugar	Ash	Insol. mat.
I. Singapore	86·73	0·46	0·42	8·00	5·40	0·39	1·37
II. Singapore	81·83	0·41	0·32	11·63	5·14	0·40	1·44
III. Singapore and Straits	78·97	0·46	0·26	9·91	7·77	0·27	1·14
IV. Bahamas	85·87	0·33	0·56	7·96	2·78	0·38	1·39

I. average of 10 samples known to be preserved in their own juice; II. preserved with addition of cane sugar; III. and IV. commercial samples, III. apparently containing added sugar, IV. probably without added sugar.

The flavour of pine-apples can be imitated by a solution of ethyl butyrate in alcohol (Hofman, Annalen, 81, 87) H. I.

PINE-NEEDLE OIL *v.* Oils, Essential.

PINE OIL *v.* Oils, Essential.

PINE RESIN *v.* Resins.

PINNOITE *v.* Heintzite.

PINOL. A tarry product of black spruce used in stables as a disinfectant.

PINTADOITE. A hydrated vanadate of calcium, $2CaO·V_2O_5,9H_2O$, occurring as a thin, green efflorescence on the sandstone cliffs of Cañon Pintado, San Juan Co., Utah. Under the microscope it is slightly pleochroic, and has moderate to high birefringence. It dissolves slowly in cold water (F. L. Hess and W. T. Schaller, 1914). L. J. S.

PINUS SYLVESTRIS OIL *v.* Oils, Essential.

PIPE-CLAY *v.* Clay.

PIPECOLINE. α-Methyl-piperidine.

PIPERAZINE (*Ethylene-imine*; *Diethylene-diamine*), Hexahydroparadiazine, also known as *Dispermine* or *Arthriticine* $(C_2H_4NH)_2$, was discovered by Cloez in 1853 and first obtained pure by Magert and Schmidt in 1890.

Ammonia is allowed to act upon ethylene bromide or chloride when a mixture of bases is formed consisting of ethylene- and triethylene-diamine, diethylene- and tetraethylene-triamine and diethylene diamine. The last-named is separated from the other salts by treating the mixture with excess of sodium or potassium nitrite and heating to 60°–70°. Dinitrosopiperazine, m.p. 154°, separates as a scaly crystalline mass readily soluble in hot water. The nitroso compound on being treated with concentrated acids or reducing agents yields ammonia and salts of piperazine from which the pure base is obtained by distillation with alkalis,

or a mixture of ethylene bromide, aniline and anhydrous sodium carbonate is heated to gentle boiling for 5 to 6 hours, the warm fused mass is extracted with hot water and the crude diphenyl-piperazine transformed into its nitroso-derivative by suspending it in cold concentrated hydrochloric acid and adding sodium nitrite solution. The precipitate is added to a 40 p.c. solution of sodium hydrogen sulphite and the suspension warmed to 80°; the solution is made strongly alkaline with sodium hydroxide and concentrated by distillation. The piperazine is finally isolated by distilling the residue with superheated steam and is absorbed by hydrochloric acid (Pratt and Young, J. Amer. Chem. Soc. 1918, 40, 1428).

It is also obtained by the reduction of ethylene oxamide with zinc dust or sodium (D. R. P. 66461); by heating disulphone piperazides with sulphuric acid at 200°–250° and subsequently treating the product so obtained with powdered sodium hydroxide (Eng. Pat. 7120; J. Soc. Chem. Ind. 1893, 545; D. R. P. 100232); by the decomposition of dibenzyl-piperazine with dilute sulphuric acid at 100° (D. R. P. 98031; Chem. Zentr. 1898, ii. 743); by heating sodium ethylene glycollate with acid derivatives of ethylene diamines at 250°–350° (D. R. P. 67811); and by heating α- or β- dinaphthyl piperazine with acids or with solutions of calcium or zinc chloride (D. R. P. 79121). For other methods of preparing piperazine, compare D. R. PP. 73354, 70055; 70056; 73125; 74628; 60547; 63618; 65347; 71576; 77351; 83524; 59222.

Properties.—Piperazine forms lustrous glassy tablets, m.p. 104°; b.p. 146°; readily soluble in water but less so in alcohol. It is very hygroscopic, forming a sesquihydrate, $C_4H_{10}N_2,6H_2O$, m.p. 44°, b.p. 125°–130°, which, on distillation above 135°, yields the pure anhydrous base (Berthelot, Compt. rend. 1899, 129, 687; *see* also Magert and Schmidt, Chem. Soc. Proc. 1893, 35).

Piperazine readily absorbs carbon dioxide, forming the compound $C_5H_{10}N_2O_2$ (Rosdalsky, J. pr. Chem. 1896, [ii.] 53, 19). Piperazine is a strong base forming crystalline salts with acids of the type $C_4H_{10}N_2,2A$ (Herz, Ber. 1897, 30, 1584). Its aqueous solution is precipitated by mercuric chloride, Nessler's solution, copper sulphate, picric acid, potassium bismuth iodide, and by gold and platinic chlorides. It also combines with bismuth chloride (Vanino and Hartl, Arch. Pharm. 244, 216). In its chemical and physical properties it is very similar to spermine, with which it was at one time thought to be identical. Piperazine is readily oxidised by potassium permanganate in the cold; it is non-poisonous and has no caustic action, and owing to the ease with which it forms a readily soluble urate, it is employed in gout and similar manifestations of uric acid diathesis (Riesenthal, Virchow's Archiv. 137, 51; Ber. 1891, 24, 241; 1897, 30, 1584). It is also used for the relief of irritation of the bladder due to excess of uric acid in the urine. Piperazine can be identified in urine by its characteristic lemon-yellow picrate (Riesenthal, Chem. Zentr. 1893, ii. 624) or by adding a slight excess of caustic soda, heating the solution, cooling, and filtering. The filtrate is acidified with hydrochloric acid and potassium bismuth iodide is added, when a brick-red precipitate consisting of characteristic microscopic crystals separates.

Piperazine is best preserved in a solution of 20 parts alcohol and 80 parts water. Like piperidine, piperazine reacts with isatin, forming blue additive compounds (Liebermann and Kraus, Ber. 1907, 40, 2492). It also forms additive compounds with quinols and phenols (Stevignon, Bull. Soc. chim. 1910, [iv.] 7, 922) and with aldehydes, carbon disulphide and carbonyl chloride (Herz, *l.c.*).

Piperazine combines with diiodo- or dibromo-pentane when they are heated together on the water-bath, forming diethylene dipiperidyl halide (Braun, Ber. 1907, 40, 2935).

***n*-Dibromopiperazine** is obtained by the action of hypobromous acid on piperazine and treating the product with dilute alkali or piperazine. It forms yellow, transparent short prisms which, without melting, are dangerously explosive at 79°–80°. It readily combines with two molecules of hypobromous acid to form a comparatively stable additive compound which explodes at 72° without melting (Chattaway and Lewis, Chem. Soc. Trans. 1905, 951). Periodides have been obtained by Linarix, J. Pharm. Chim. 1909, [vi.] 30, 241.

α-2 : 5-Dimethyl piperazine, m.p. 118°–119°, b.p. 162°, is formed by the reduction of 2 : 5-dimethyl pyrazine or of lactimide with sodium and alcohol (Hayer, Zeitsch. physiol. Chem. 34, 347); or it is isolated from commercial amyl alcohol by treating it with sodium (Bamberger and Einhorn, Ber. 1897, 30, 226). It is alkaline, readily soluble in water and in alcohol, and sublimes at ordinary temperature. The β-compound has m.p. 114°–115°, b.p. 162°.

α-Dimethylpiperazine tartrate or **Lycetol**, $C_6H_{14}N_2{\cdot}C_4H_6O_2$, m.p. 250°, is a white crystalline powder having an acid reaction. It is readily soluble in water, is less hygroscopic than piperazine, and its solution is more stable than that of the latter. It also has a more agreeable taste than piperazine itself.

Piperazine benzoate, glistening plates, subliming at 120°, and the **salicylate**, fine white needles subliming at 160°, are formed by mixing alcoholic solutions of the base and acid. The former is alkaline and the latter neutral to helianthin but both are acid to phenolphthalein (Astruc, Bull. Soc. chim. 1906, [iii.] 35, 169). They can also be formed by fusing the two substances together and recrystallising from the above solvent (Eng. Pat. 25905; J. Soc. Chem. Ind. 1897, 933; Pharm. Zeit. 43, 319).

The **tartrate** and **citrate** (Eng. Pat. 26078; J. Soc. Chem. Ind. 1898, 68), which are non-hygroscopic and may be dried at a high temperature, and also the **quinate** (Eng. Pat. 11420; J. Soc. Chem. Ind. 1899, 856) are produced similarly. Piperazine also forms acid salts with oxalic, tartaric and citric acids which yield useful neutral double salts with lithium (Eng. Pat. 18981; J. Soc. Chem. Ind. 1896, 758).

Piperazine cacodylate

$$AsOMe_2(OH)_2C_4H_{10}N_2{\cdot}4H_2O$$

obtained by adding piperazine (1 mol.) to cacodylic acid (2 mols.). Colourless crystals, m.p. 54–55°. Its aqueous solvent gives a white precipitate with mercuric chloride, a brown precipitate with iodine in potassium iodide, and

yellow precipitates with picric acid or uranium acetate. Is acid to phenolthalein, and alkaline to helianthin A.

Piperazine mercuric citrate is formed by mixing together piperazine and mercuric citrate in absolute alcohol. It crystallises in white needles sintering at 100°, m.p. 137°, and forms a strongly alkaline solution in water.

Piperazine mercuric acetate is formed similarly, is fairly soluble in water, darkens at 188° and has m.p. 198°.

Both these salts, as also the corresponding mercuric-*sulphate-cyanide* (m.p. 144°–145°) *-benzoate* (m.p. 107°–108°) *-salicylate* and *nitrate* and also the corresponding *diethylpiperazine mercuric nitrate* (m.p. 148°–151°), *-sulphate* (m.p. 124°–125°), *-cyanide* (m.p. 159°–160°), *-succinate* (m.p. 108°–110°) and *-salicylate* (m.p. 128°–130°) have antiseptic properties and do not coagulate albumen. They can also be prepared by treating the mercuric salt with the carbonate of the organic base (D. R. P. 125095, 1902).

Piperazine theophylline is formed by combining molecular proportions of its components or their salts. It has an alkaline reaction, is sparingly soluble in alcohol but readily so in water (D. R. PP. 214376, 217620, 224981 ; J. Soc. Chem. Ind. 1910, 1134).

Piperazine cinchonate or **sidonal**

$$C_4H_{10}N_2(C_7H_{12}O_6)_2$$

m.p. 168°–171°, is a colourless crystalline powder having an acid taste and reaction and is readily soluble in water (Pharm. Zeit. 45, 182).

α-Piperazine anthraquinone, formed by the action of nitroanthraquinone on the base, separates from methyl alcohol in orange-red crystals (D. R. PP. 136777, 136778, 1903).

Nitrosopiperazine $C_4H_8N_2(NO)_2$ formed by adding sodium nitrite to a solution of piperazine hydrochloride and warming the mixture ; it crystallises from water in yellowish lustrous plates, m.p. 158°, and gives the Liebermann reaction with phenol and sulphuric acid.

Diphenyl piperazine, m.p. 163·5°, is formed by the action of ethylene bromide on aniline, sufficient dry sodium carbonate or acetate being added to fix the hydrogen bromide produced. It combines with a number of diazo and diazosulphonic compounds yielding yellow-red and violet dyes for cotton, wool, and silk (Bischoff, Ber. 1889, 22, 1777).

Piperazine forms phosphates and arsenates of the type $C_4H_{10}N_2,H_3PO_4,H_2O$;

$$C_4H_{10}N_2,2H_3PO_4$$

(Astruc and Brenta, Bull. Soc. chim. 1908, [iv.] 3, 963), and also glycero- phosphates (Astruc, Compt. rend. 1905, 140, 727).

A large number of other piperazine derivatives have been prepared (Ladenburg, Ber. 1891, 24, 2400 ; Bischoff and Nastvogel, *ibid.* 1889, 22, 1783, 1792 ; Bischoff and Trapesonzjanz, *ibid.* 1892, 25, 2940 ; Wolff, *ibid.* 1893, 26, 721 ; Herz, *l.c.* ; Stoehr, J. pr. Chem. [ii.] 47, 439 ; *ibid.* 48, 191 ; Cazeneuve and Moreau, Compt. rend. 1897, 125, 1182 ; *ibid.* 1898, 126, 1802 ; Rijn, Chem. Zentr. 1898, i. 380 ; Knorr, Ber. 1904, 37, 3507 ; *ibid.* 1905, 38, 3136 ; *ibid.* 1906, 39, 1420 ; Astruc, Bull. Soc. chim. 1905, [iii.] 33, 839 ; Borsche and Titsingh, Ber. 1907, 40, 5008 ; Van Dorp, Rec. trav. chim. 1909, 28, 18 ; Franchimont, *ibid.* 1910, [ii.] 14, 296 ; Franchimont and Kramer, *ibid.* 1912, 31, 40 ; Datta and Choudhury, J. Amer. Chem. Soc. 1916, 38, 1079 ; Astruc, Bull. Soc. chim. 1916, [iv.] 19, 392).

Piperazines are the derivatives of the ring $N<\begin{matrix}C\cdot C\\C\cdot C\end{matrix}>N$. They are formed by the methods given above and also by the reduction of the corresponding pyrazines with sodium and alcohol. They form strong colourless bases, some liquid and some crystalline ; they fume slightly in air and readily absorb carbon dioxide. The piperazines form hydrates which are readily soluble in alcohol or chloroform but sparingly soluble in water. The poly-substituted pyrazines always give 2 isomeric piperazines on reduction. The lower piperazines have higher boiling-points than the corresponding pyrazines, whilst for the higher compounds this relation is reversed (Stöhr, J. pr. Chem., 1897, [ii.] 55, 49).

PIPERIC ACID *v.* RESINS.

PIPERIDIN *v.* RESINS.

PIPERIDINE *v.* BONE OIL.

PIPERIDINE GUIACOLATE *v.* BONE OIL.

PIPERINE $C_{17}H_{19}O_3N$, the alkaloid contained in the fruits of *Piper nigrum* (Linn.), as well as in other plants belonging to the natural order *Piperaceæ, e.g. Piper longum* (Linn.), *P. Clusii* (C. DC.), *P. methysticum* (Forst.), &c. Commercial black and white peppers contain from 5 to 9 p.c. of this alkaloid (*v.* PEPPER).

Preparation.—Piperine may be extracted from finely-powdered pepper, preferably white pepper, by means of alcohol. The alcohol is distilled from the solution, and the alkaloid precipitated from the remaining aqueous residue by adding excess of potash, so that the greater part of the resin is dissolved. The base is purified by crystallisation from alcohol.

Another plan is to mix the powdered pepper with milk of lime and boil the mixture for about 15 mins. ; it is then evaporated to dryness on the water-bath. The free piperine is extracted from the dry mass by means of boiling ether and crystallised from alcohol (Cazeneuve and Caillot, Bull. Soc. chim. 1877, [ii.] 27, 290). This process is also employed for the estimation of piperine in pepper.

Properties.—Monoclinic crystals, m.p. 128°-129°. Slightly soluble in water, more soluble in ether, alcohol, benzene, or chloroform. Optically inactive. An alcoholic solution has a pepper-like flavour. Piperine is a weak base. It is not alkaline, and may be extracted from solutions in dilute acids by indifferent solvents, such as ether. The principal salts are formed by combination with acids in the absence of much water. The platinichloride and mercurichloride are crystalline and insoluble in water ; the triiodide $B_2\cdot HI,I_2$, formed by adding iodine in potassium iodide to a solution of piperine in alcohol containing hydrochloric acid, forms steel-blue needles.

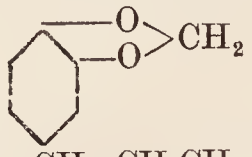
Reactions and constitution.—Piperine dissolves in strong sulphuric acid, forming a dark red solution. Nitric acid converts the alkaloid into a resinous mass, which dissolves in potash, producing a dark red solution.

When piperine is heated with aqueous alkalis it is hydrolysed into piperidine and piperic acid

$$C_{17}H_{19}O_3N+H_2O=C_5H_{11}N+C_{12}H_{10}O_4$$

Piperidine is hexahydropyridine, whilst piperic

acid is a derivative of protocatechuic acid having the following constitution—



$CH : CH \cdot CH : CH \cdot CO_2H$

Piperic acid.

Piperine has been prepared by the action of piperyl chloride on piperidine (Rugheimer, Ber. 1882, 15, 1390), and Ladenburg and Scholz have prepared piperic acid from protocatechuic aldehyde (*ibid.* 1894, 27, 2958). Piperine is therefore piperylpiperidine (*cf.* Dobbie and Fox, Chem. Soc. Trans. 1913, 103, 1193).

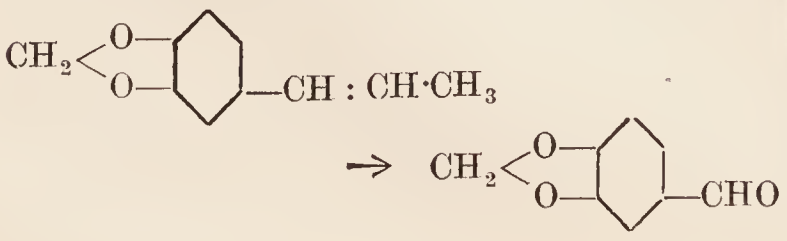
PIPERITONE, $C_{10}H_{16}O$, or *d*-Δ'-*p*-menthen-3-one, an unsaturated ketone, possessing a peppermint smell and taste, characteristic of the essential oil of a group of eucalypts known in Australia as 'Peppermints.' *e.g. E. hæmastoma, E. dives, E. piperita,* &c., found in New South Wales and Victoria. Appears generally to occur in association with *l*-α-phellandrene, and with the corresponding secondary alcohol, piperitol. Piperitone is a colourless liquid which gradually turns yellow. D_4^{20} 0·9348; n_D^{20} 1·4837; b.p. 106–107/10 mm., 229°–230°/760. May readily be oxidised to thymol, or reduced to menthone (Smith and Penfold, J. Proc. Roy. Soc. N. S. Wales, 1920, 54, 40; Read and Smith, Chem. Soc. Trans. 1921, 779). The main constituent (about 80 p.c.) of the oil of *Andropogon iwarancusa,* Jones, is *d*-piperitone (Simonsen, Trans. Chem. Soc. 1921, 119, 1644).

PIPERNO *v.* TRACHYTE.

PIPERONAL (*Piperonaldehyde Heliotropine*) methylene-proto-catechuic aldehyde

$$CH_2O_2 : C_6H_3 \cdot CHO$$

was first obtained by Fittig and Mielk (Annalen. 1869, 152, 35) by the oxidation of piperinic acid, and its constitution was established by Fittig and Remsen (*ibid.* 1871, 159, 158). It is closely connected with various natural products including piperine, safrol and *iso*safrol, from all of which it may be obtained on oxidation. Piperonal itself occurs only to a limited extent in nature, being generally found in conjunction with vanillin and other alkyl-oxyaldehydes; it is found in small quantities in spiraea oil and also in certain vanilla fruits such as the vanillon or pompona (Göller, Chemist and Druggist, 1907, 65, 13). For its preparation from camphor oil, *see* Nagoi (J. Chem. Ind. Tokyo, 1920, 23, 56, 151). It has not been proved whether the characteristic smell of the flowers of the heliotrope variety, from which the commercial name is derived, is actually due to this compound. Piperonal, although not used in the preparation of scents and essences, is employed considerably for the purpose of soap perfumery and is now prepared in large quantities, especially by Schimmel and Co., by the oxidation of *iso*safrol (Bericht von Schimmel & Co., April, 1893).



Otto and Verley have proposed to obtain piperonal by the action of ozone on safrol or *iso*safrol (D. R. P. 97620).

Properties and reactions.—White crystals, m.p. 37°, b.p. 263°, very slightly soluble in water, easily so in most organic solvents. With dilute hydrochloric acid, protocatechuic aldehyde is formed and carbon is said to be liberated. According to Schut (Chem. Zentr. 1910, i. 1829), the reaction is much more complicated; with phosphorus pentachloride there is formed piperonal chloride $CCl_2O_2 : C_6H_3 \cdot CHO$; with sulphur chloride the reaction proceeds more smoothly; with water this compound yields quantitatively protocatechuic aldehyde, so that this is a satisfactory method of preparation from piperonal (Schimmel & Co., D. R. P. 165727); with sodium amalgam there is formed piperonyl alcohol and two isomeric hydropiperoins; aniline condenses to form piperonal anilide; ammonium sulphide forms dithiopiperonal; acid sodium sulphite forms an addition compound, as also does trinitrobenzene. By condensation with α-bromopropionic ester, piperonal may be converted into an acid which loses carbon dioxide, forming *iso*safrol (Wallach, Annalen, 1897, 357, 72). For derivatives, *see* Rilliet and Kreitmann (Compt. rend. 1913, 157, 782); Graziani (Atti R. Accad. Lincei, 1913, [v.] 22, 623); Graziani and Bovini (*ibid.* 1913, [v.] 22, i. 793); Angeli and Alessandri (*ibid.* 1913, [v.] 22, i. 735); Bovini and Graziani (Gazz. chim. ital. 1913, 43, ii. 674); Brady and Dunn (Chem. Soc. Trans. 1915, 1858); Henderson and Heilbron (*ibid.* 1915, 1748); Orr, Robinson and Williams (*ibid.* 1917, 946); Robinson (*ibid.* 1917, 120); Weinhagen (*ibid.* 1918, 585); Wilkendorf (Ber. 1919, 52 [B], 606).

PIPEROVATINE $C_{16}H_{21}O_2N$ occurs in *Piper ovatum* (Vahl.). Forms colourless needles, m.p. 123°, from alcohol by addition of ether. Optically inactive and feebly basic. Heated with water at 160° it gives a volatile base, probably a pyridine derivative, an acid and a substance having an odour of anisole. It is a temporary depressant of motor and sensory nerves and sensory nerve terminations, producing some local anæsthesia. It behaves as a heart poison and stimulates the spinal cord in frogs, causing tetanic spasms somewhat resembling those induced by strychnine (Dunstan (with Garnett), Chem. Soc. Trans. 1895, 67, 94; (with Carr), Chem. Soc. Proc. 1895, 177). It closely resembles *pellitorine* (pyrethrine), the alkaloid of pyrethrum root (*Anacyclus Pyrethrum* [DC.]) (Dunstan and Garnett, *l.c.* 101; *cf.* Buchheim, Arch. expt. Path. Pharm. 1876, 5, 458).

PIRAL. Syn. for pyrogallol.

PISANGCERIC ACID $C_{23}H_{47}COOH$, m.p. 71°, is obtained from Pisang wax, *v.* WAXES.

PISANG WAX *v.* WAXES.

PISOLITE *v.* OOLITE.

PISTACHIA LENTISCUS *v.* SUMACH.

PITCH. Various substances met with in the organic kingdom when submitted to destructive distillation yield, in addition to fluid products, a residuum that on cooling assumes a more or less viscous or solid character; and, furthermore, at various places on the earth's surface extensive deposits are found consisting of black, resinous substances of similar appearance and properties. To these products have

been assigned the terms of 'pitch,' 'bitumen,' and 'asphaltum.' Each of these substances possesses distinctive features, and each in its place fulfils important requirements in the arts.

Bitumen, asphaltum, mineral pitch. These compounds consist of complex mixtures of hydrocarbons, and are found in many localities and under the most varied conditions. Probably the celebrated Pitch lake, situated in the island of Trinidad, and said to be upwards of three miles in circumference, represents one of the most important deposits of natural bitumen known, although additional sources have been found in Cuba, Central and South America, California, Arkansas, Nicaragua, and Peru, in India, Palestine, Egypt, Turkey, Italy, France, Germany, Switzerland, Ho-Tsing, province of Szu-Tehuan, China, and Asiatic Russia.

The origin of these deposits is involved in considerable obscurity; they appear to have been formed from the unsaturated hydrocarbons in petroleum. Bitumen has been regarded either as a product of chemical action or as a distillate produced by natural causes from animal and vegetable remains. It has been argued that if the bitumen were the result of a purely chemical process, we should expect to find a generic uniformity in the character of the substance wherever found on the earth. On the other hand, if petroleum is the result of metamorphism, its generation is co-existent only with that of metamorphic actions. If we accept this hypothesis, the generation of petroleum must be considered as practically ended.

In studying the asphalt of Bentheim, Patrono, Castro, Colla San Magna, and other places, the conclusions arrived at have confirmed the views of Mendeléeff to the effect that their formation has been brought about by inorganic means. Bitumen is frequently met with in places where, from a geological point of view, its occurrence can be explained only by assuming that it has accumulated within the fissures in the same manner as that contained in lavatic geodes, and separated from prehistorical tufaceous deposits by inorganic means. Engler, who has given some considerable study to the Bentheim asphalt, furnishes the following particulars respecting it. It is insoluble in alcohol, ether, carbon disulphide, oil of turpentine, and similar solvents, but melts when strongly heated: sp.gr. 1·092. It contains:

	I.	II.
Carbon	89·46	89·83
Hydrogen	9·55	9·88
Ash	1·09	1·14

Distillation yielded the following products:—

	I.	II.
Tar	36·8	38
Coke	48·9	48
Gas and water	14·3	14

The tar obtained by the distillation of the asphalt on a large scale was free from phenol and creosotic compounds, and the products of its distillation were as follows:—

	p.c.
Burning oils	12·72
Gas and lubricating oils	9·78
Paraffin	1·50
Paraffin grease	0·65
Coke from retorts	46·09
Coke from tar	0·86
Pitch	1·52
Loss, gas and water	26·88
	100·00

Egyptian asphalt contains:

	p.c.
Carbon	85·29
Hydrogen	8·24
Oxygen	6·22
Nitrogen	0·25

The bitumen of Judea, found floating on the Dead Sea, contains:

	p.c.
Carbon	77·84
Hydrogen	8·93
Oxygen	11·54
Nitrogen	1·70

Sulphur is invariably present in natural bitumens, varying in quantity from 3 to 10 p.c.; from such samples, hydrogen sulphide is always given off on heating. Asphaltums and bitumens vary considerably in character. Generally, their appearance is that of a smooth, hard, brittle, black, or brownish-black resin, breaking with a distinct conchoidal fracture: the sp.gr. varies from 1 to 1·7; when free from mineral matter they may be even lighter than water. When distilled with water, asphaltum yields a volatile oil called by Boussingault 'petrolene,' probably consisting of a mixture of paraffins. The residue of 'asphaltine,' which remains when the petrolene is completely driven off, is a solid black substance resembling the original substance prior to distillation, but which does not soften below under about 300°, and decomposes below its fusing point.

Trinidad pitch yields, when heated—

	p.c.
Volatile organic matter	76·75
Non-volatile organic matter	17·77
Ash	5·48
	100·00

Natural bitumen is only partially soluble in alcohol, but more completely so in carbon disulphide, carbon tetrachloride, petroleum spirit, chloroform, oil of turpentine, coal-tar, benzene and naphthas; the pyridine bases, also derived from coal-tar, scarcely act upon it. The portion, however, that passes into solution communicates a strong greenish fluorescence to the liquid, and when examined spectroscopically, in the manner described for examining crude anthracenes for certain impurities (Chem. News, 26, 199; 31, 35, 45), two distinct absorption bands are visible near the D line of the spectrum, from yellow to green, which distinguishes it from all other pitches, coal-tar excepted, which occasionally shows bands, but invariably situated in the blue portion of the spectrum near the F and G lines.

In petroleum spirit, 74·23 p.c. of its organic matter is soluble and 20·29 p.c. insoluble.

At a temperature varying from 58° to 60° bitumen softens, and it melts at about 100°, although varieties are met with that melt only at a much higher temperature.

The following table of results obtained by A. E. Jordan and given in Allen's Organic Analyses shows the difference between natural asphalts and artificial products:—

Material	Ash	Organic matter		Action of petroleum spirit		
		Volatile	Non-volatile	Soluble	Insoluble	Percentage of organic matter soluble
Asphalt (origin unknown) .	0·60	80·79	18·61	47·63	51·77	47·91
Trinidad pitch . . .	5·48	76·75	17·77	74·23	20·29	78·53
Petroleum pitch . . .	none	50·43	49·57	36·16	63·84	36·16
Shale oil pitch . . .	0·25	66·40	33·35	63·62	36·13	68·77
Coal-tar pitch . . .	0·15	49·33	50·52	18·56	81·29	18·58
Bone pitch (inferior) . .	0·33	56·15	43·52	29·96	69·71	30·05

Boussingault's methods are not now used and the terms petrolene and asphaltene used by him have received another significance, that portion soluble in petroleum spirit, ether, or acetone being known as petrolene and the portion insoluble in any of these liquids but dissolved by boiling turpentine or cold chloroform being known as asphaltene.

Applications of asphaltum.— The purer asphaltums are employed almost exclusively for the manufacture of black varnishes and japans, for which purpose they are eminently adapted, yielding surfaces and coatings of great brilliancy and not prone to 'break up' or disintegrate. Asphaltum selected for the purpose of the varnish maker should be practically free from mineral matter or within a limit of 5 p.c., it should be completely soluble in carbon disulphide, chloroform, high boiling coal-tar naphtha, and oil of turpentine (mineral matter excepted). It should break with a conchoidal fracture and brilliant lustre. It should not flow or lose shape, like wood tar and many of the fatty pitches, when left on a plane surface, and an angular fragment should retain its shape and the sharpness of its angles in boiling water.

Asphalt rock. Asphaltum is often met associated with sand or limestone or the two variously admixed; in this condition the mineral is known as 'asphalt rock,' and occurs in the upper Jurassic formation interstratified with ordinary limestone.

The following figures, by Durant Claye, show the proximate composition of some rock asphalts employed for paving:—

—	Val de Travers Switzerland	Lobsann Alsace	Seyssel Ain France	Maestu Spain	Ragusa Sicily
Water and other matter volatilised at 100°C.	0·35	3·40	0·40	0·40	0·80
Bituminous matter	8·70	11·90	9·10	8·80	8·85
Sulphur in organic combination or free state	0·08	4·99	—	trace	—
Iron pyrites	0·21	4·44	—	—	—
Alumina and oxide of iron . .	0·30	1·25	0·05	4·35	0·90
Magnesia	0·10	0·15	0·05	3·85	0·45
Lime	49·50	38·90	50·50	5·70	49·00
Carbon dioxide	40·16	31·92	39·80	8·15	39·40
Combined silica	—	—	—	11·35	—
Sand	0·60	3·05	0·10	57·40	0·06
	100·00	100·00	100·00	100·00	100·00

Native calcareous asphalt exhibits a brown or nearly black colour and breaks without evidence of cleavage. The fracture is earthy and granular, not unlike chocolate, both in appearance and colour. When long exposed to the air it loses this character and then resembles ordinary limestone: this change, however, only extends to the surface.

The specific gravity of rock asphalt is about 2·23. It is hard and may be broken with a hammer, but when warmed it may be softened to a kind of paste and at about 60° falls to powder.

Good rock asphalt is homogeneous in structure and shows no indication of contained limestone. It is frequently veined, and contains

large crystals of calcite impregnated with bitumen; this feature is considered an important indication, bad specimens or low qualities showing an absence of such impregnation, which renders them difficult to manipulate. Val de Travers, Seyssel, and other asphalt rocks, when employed for paving, are melted with definite proportions of good native material, such as Trinidad pitch. The product of this mixture is technically known as 'mastic,' and in using it further additions of bitumen, shale oil, and grit are frequently made:

The following analysis by Durant Claye will convey a general idea of these compositions:

	Refined bitumen from Bastennes	Imitation asphalt made from coal-tar
Moisture	0·30	0·60
Bituminous matters soluble in carbon disulphide . .	69·35	20·65
Organic matter insoluble in carbon disulphide . .	4·40	18·45
Alumina and oxide of iron .	2·85	2·65
Magnesium and calcium carbonates	2·65	39·60
Silica	20·35	18·05
	100·00	100·00

For determining the actual bituminous matter in asphaltic rocks, natural and otherwise, the air-dried sample is exhausted with suitable solvents, which may consist of carbon disulphide, Russian oil of turpentine or coal-tar benzene. The operation may be conducted in a Soxhlet's tube, and if a correction be made for the moisture expelled at 100° the loss of weight furnishes the quantity of bitumen removed. The determination may be further checked by distilling off the solvent and weighing the residue, observing the usual precaution of drying at 100° until constant in weight. The bitumen thus obtained should be heated further to 220°, when, if the sample is good, there will be little or no further loss of weight; if, however, volatile oils or petroleum be present, the loss may be considerable.

The volatile oil is best determined by repeatedly digesting the powdered sample with cold alcohol and weighing the residue; the exhaustion may be considered as complete when a portion of the alcoholic washing shows no turbidity on dilution with water.

If the residue left after exhaustion exhibits a dark colour, other organic constituents of valueless nature are present. Their proportion may be ascertained by igniting the weighed residue left after the removal of the bitumen, re-carbonating it with ammonium carbonate, again gently igniting it and re-weighing. The loss of weight represents the quantity of non-bituminous matter present.

Val de Travers asphalt gives up the whole of its organic matter to petroleum spirit, imparting a deep brown colour to the fluid, perfectly free from fluorescence, whereas the soluble portion of coal-tar pitch does not exceed 20 or 25 p.c., yielding a solution exhibiting a deep greenish fluorescence, a characteristic of this pitch in any of its solvents and which renders its detection alone or in admixture a matter of no great difficulty (*v. infra*).

Pitches derived from technical processes.

Artificial pitches. Coal-tar pitch may be looked upon as occupying the most prominent position in the series, both as regards the magnitude of its production and its corresponding consumption for the purposes of artificial fuel, asphalts and varnishes.

Coal-tar pitch is the residue remaining in the stills after separation of the various fractions known as naphthas, light oils, carbolic, creosote and anthracene oils, and amounts to about two-thirds of the weight of the tar operated upon. Its physical character is mainly dependent upon the temperature employed in distillation; but its ultimate chemical composition is more or less governed by the quality and composition of the coal distilled. It may be either 'soft' or 'hard' or 'medium'; it may be either 'normal,' as a product resulting from the simple distillation of tar, or it may be otherwise, as when mixed with green or other tar oils before running from the stills. The selection of tar distillates to be used in thus thinning down a pitch carried to a full limit of distillation is important, as it has been found that when creosote or naphthalene is employed, a pitch is obtained lacking in binding or cementing power, and blocks or briquettes made from it are liable to crumble. This defect is only obviated by the use of the heavier distillates, such as green oils which are of a more viscid and adhesive character.

When pitch is passed through a red-hot tube it yields about 250 times its bulk of gases, chiefly hydrogen.

Pitch may be utilised by burning it into lamp-black, and, according to Thenius, 500 kilos. of pitch yield 200 kilos. of varying descriptions of lamp-black and 200 kilos. of coked residue.

Referring more generally to the several results that may be obtained by varying the fractions during the distillation of coal-tar, it may be stated that if the operation be terminated at the point at which the light oils only are driven off, the residue in the still, representing about 80 p.c. of the charge, may be used for the preparation of asphalts, under the name of 'refined' or 'prepared' tar, although it is very doubtful whether material of this character is to be met with in the present day. If about 10 p.c. more is run off, the residue is soft pitch; moderately hard and hard pitch follow, the latter when the distillation is carried on as far as practicable in wrought-iron stills. The 'asphalt prepared' or 'refined tar' thus obtained by simply distilling off the naphthas and light oils, invariably contained all the constituents of the distillate that would follow if carried to its limit and collected apart, *i.e.* creosote oils, phenols, naphthalene, anthracene and higher boiling-point substances. Coal-tar pitch in its normal condition and as originally obtained, is a bright, black, lustrous substance, breaking with a well-marked conchoidal fracture; but as now met with it presents a more or less dull or greyish tint, due to the altered condition under which it is obtained. These

are, firstly, distillation, in which steam, either superheated or otherwise, is injected into the still during the operation, and by which it can be pushed to a greater limit and more complete extraction of anthracene, without endangering the still; and, secondly, the admixture of the residual pitch with 'green' or other oils, in order to bring it to a consistency at which it may be run off with facility and yield a product that shall represent 'soft,' 'medium,' or 'hard' pitch at will.

Coal-tar pitch invariably contains some of the higher boiling hydrocarbons of coal-tar, notably anthracene, phenanthrene, pyrene, chrysene, together with bitumen and free carbon. The ultimate percentage composition of coal-tar is given by Habets as:

	p.c.
Carbon	75·32
Hydrogen	8·19
Oxygen	16·06
Ash	0·43
	100·00

Small proportions of sulphur and nitrogen are also present, the former to the extent of 0·4–0·7 p.c. Treated successively with cold benzene, carbon disulphide, boiling benzene, and boiling alcohol, Behrens obtained 23·54 p.c. of a black powder resembling anthracite and containing 91–92 p.c. of carbon, 3·1 p.c. of hydrogen, and 0·4–0·9 p.c. of ash.

Donath and Asriel (Chem. Zentr. 1903, i. 1099) give the following figures:—

—	C	H	N	S	Extract with			Residue
					Petroleum spirit	Benzene	CS_2	
Soft pitch	91·80	4·62	?	?	25·05	44·98	6·57	22·82
Medium pitch	94·32	3·98	0·148	0·77	15·14	40·03	7·10	38·16
Hard pitch	93·16	4·36	?	?	15·51	39·46	5·21	29·39

The extractions with benzene and carbon disulphide followed in rotation.

The specific gravity of hard pitch varies from 1·475 to 1·300. It is wholly insoluble in water but partially soluble in alcohol and more so in benzene or carbon disulphide. Cold petroleum spirit exerts but little solvent action upon it, but when heated it dissolves it to the extent of 18 to 23 p.c. The pyridine bases also dissolve the soluble organic matter from pitch, but somewhat tardily, and only with the assistance of heat.

Solutions of coal-tar pitch exhibit a deep yellow or yellowish-green fluorescence, which is highly characteristic of that substance. When heated it exhales an odour equally characteristic and not easily mistaken for any other known pitch. The proportion of volatile organic matter given off on heating ranges from 46 to 64 p.c.

A benzene solution of coal-tar pitch when examined spectroscopically shows a cutting out of the blue and violet portions of the spectrum, with occasional absorption bands between the F and G lines.

Testing of pitch.—For the requirements of commerce, pitch has to be tested for its 'softening' and 'melting' point, and contract notes stipulate that a sample is to 'twist' fairly after immersion for two minutes in water at 60° but not under 50°, must contain at least 53 p.c. of 'volatile organic matter,' and must be free from any extraneous matter such as grit or sand.

The twisting and melting-point of pitch are ascertained by methods of comparative simplicity, only varying in trifling points and details. Probably the simplest and most readily followed is that of F. G. Holmes, and is conducted in the following manner:

Several pieces of pitch are selected from different parts of the sample and cut to the size of half-inch cubes. These cubes are then supported on metal wires by heating the ends of the wires and pressing them into the pieces of pitch, which are then suspended in a vessel containing about 500 c.c. of water heated by any convenient means, at a uniform rate of 5° per minute, as indicated by a thermometer immersed in the water with the bulb about two inches from the bottom of the vessel.

The cubes are suspended on a level with the bulb of the thermometer. As the temperature rises the pieces of pitch are removed from time to time and twisted or squeezed with the fingers and the temperature noted at which they assume the following conditions:

(1) Readily twisting or soft, *i.e.* when the pitch can be easily twisted round several times.

(2) Very soft, *i.e.* when it yields to a very light pressure of the finger.

(3) Fused, *i.e.* when the pitch melts off the wire.

Soft pitch softens at 40° and melts at about 60°.

Moderately hard pitch softens at 60° and melts at about 80°.

Hard pitch softens at 80° and melts at about 120°.

The estimation of the volatile matter is conducted in the same way as in the case of coal and other bituminous substances, viz. by heating about 1 gram of the pitch to be examined in a platinum crucible of $1\frac{1}{4}$ to $1\frac{1}{2}$ inches height with the cover on, which should have a small aperture in the centre. The heat is applied by means of a good Bunsen burner, first gently until no more smoke and vapour issue from the opening in the lid, finally as strongly as the burner will permit. The operation may last 20 minutes. The crucible is then placed in a desiccator and, after cooling, the residual coke is weighed; it ranges from 36 to 53 p.c. Fixed

carbon and coke dust may be determined by successively exhausting with benzene, carbon disulphide, and alcohol, employing a Soxhlet tube for the extraction.

Methods for testing the softening point of pitch have been described by Muck (Z. f. Berg. Hutten u. Salinenwesen, 1889); Schewk zu Schweinsberg (Zeitsch. angew. Chem. 1890, 704); Maybery and Sieplein (J. Amer. Chem. Soc. 1901, 20, 16); Kraemer and Sarnow (J. Soc. Chem. Ind. 1903, 55); Weiss (J. Ind. Eng. Chem. 1916, 8, 841); Mansbridge (J. Soc. Chem. Ind. 1918, 182 T); Spielmann and Petrie (*ibid.* 1919, 68 T); L. M. Proctor (Met. & Chem. Eng. 1919, 21, 81); Twiss and Murphy (J. Soc. Chem. Ind. 1919, 38, 405 T). Lampe suggests a standardised method. A thin-walled, open-ended glass tube of 3 or 4 mm. bore has its lower end closed by a column of the pitch 10 mm. high, introduced in the melted state and allowed to solidify. Five grams of mercury are introduced into the tube above the pitch. The tube is fastened to a thermometer and heated in water at the rate of 1°C. per minute. As the pitch softens the mercury forces its way through it, and the temperature at which drops of mercury fall from the lower end of the tube is taken as the melting-point of the pitch.

The suitability of a pitch for the purpose of artificial fuel may be ascertained by carefully distilling a given quantity of the sample in a glass retort and noting the character of the distillates; when creosote or naphthalene has been used in thinning or diluting before running from the still they are accompanied with a considerable sublimate of naphthalene passing over at a comparatively low temperature; green oils do not yield naphthalene in this manner or sublimates that may be mistaken for it (*cf.* Bernus, Bull. Soc. chim. Belg. 1911, 25, 7). Pitch intended for briquetting should be tested to ascertain: (1) the content of plastic matter; (2) the temperature at which it softens sufficiently to bind together the particles of coal; (3) the temperature at which the pitch begins to stick to the machine; (4) the percentage of ash; and (5) the percentage of volatile matter.

J. E. Mills (Bulletin 343, U.S. Geological Survey) gives the following tests employed at the U.S. Government fuel testing works, St. Louis, for the testing of briquette pitch:

1. The material is distilled; all coming over below 270° is rejected as valueless. 2. The flowing point is determined by placing about 3 c.c. of pitch in the bottom of a test-tube $\frac{1}{2}$-inch in diameter and inserting it in a bath. The temperature of the bath is raised until, on taking out the tube and inverting it, the pitch flows 1 inch down the tube in 15 seconds. This point should be not less than 70°. 3. The pitch is extracted with CS_2. The smaller the amount of residual carbon the more satisfactory the pitch. The higher the flowing point the better the briquettes stand in the fire.

Applications and uses of coal-tar pitch. Coal-tar pitch is extensively used in the manufacture of patent or artificial fuel, varnishes, japans, and asphalts, the trade in the first-named product having assumed enormous proportions. Fuel of this description consists of admixtures of coal-tar pitch with small coal or slack, compressed into the form of blocks and known under the name of 'briquettes.' This industry would seem to be due to Ferrand and Marsais who, in 1832, obtained a French patent for using coal-tar for this purpose.

Marsais, since 1842, employed soft pitch, and in that year commenced the works at Berardy, near Saint Etienne. Hard pitch was used in 1843 in England by Wylam, and since 1854 in France. The manufactured fuel was sold in that country under the name of 'peras.' The manufacture of patent fuel has opened up wide channels for the consumption not only of the immense quantities of 'slack' obtained wherever mining operations for coal are carried on, but for the almost equally large bulk of pitch resulting from the operations of the tar distiller.

In the manufacture of briquettes, certain conditions are observed, regulating shape, dimensions, and weight. The form should be that of a parallelopipedon, and they should not weigh more than 22 lbs.; they should possess a firmness approaching that of natural coal, and to attain this end the proportions of pitch used in their fabrication must be at least 5–7 p.c. They should not yield more than from 6·5 to 6·75 p.c. of ash, if intended for locomotive use, or 10 p.c. if for steamboat use.

When broken they should fracture with a clean, bright, and granular surface in the absence of which they are generally faulty. Their regular shape permits of facilities of stowage, and the loss in transit by disintegration does not amount to more than 1 or 2 p.c. against 30–50 p.c. as with coals. They should not fall to pieces in the fire but agglomerate into a firm compact coke.

Patent fuel of good quality is said to yield 10 p.c. more heating power than steam coal; it makes less dirt and when manufactured from hard pitch gives less black smoke than most kinds of coal.

In the preparation of artificial fuel of this character numerous attempts have been made to employ fatty, oily, mucilaginous, and similar substances or coal-tar, as the agglomerating or cementing medium, but the only materials now used are soft or hard pitch derived from coal-tar.

The operation of blending is comparatively simple, requiring little plant beyond that of melting pans or pug mills. Occasionally, when hard pitch is employed, a mixture of this material with coal, both in fine powder, is subjected to the action of superheated steam, by which the compound is softened and yields a compact conglomerate on cooling.

In shaping or forming such mixtures of coal and pitch into blocks or briquettes, presses with open and closed moulds are in use. The process scarcely requires description, being quite analogous to that of moulding bricks, the machine that works with dry clay being constructed with closed moulds, those for wet clay with conical mouthpieces (dies).

Black varnishes and japans.—In the preparation of varnishes, japans, and paints for coating and protecting the surfaces of iron and wood, tar pitch is simply dissolved in, or melted with, a suitable coal-tar distillate, depending on the purpose to which the product is to be applied and the rate at which it is required to

dry or become hard. These solvents vary from the more volatile benzene to the heavier xylenes or solvent naphthas, and it is not an unusual thing to employ naphthas and light oils as run from the still, up to actual creosote. No special knowledge or plant is requisite in compounding them beyond that well known to varnish makers.

As a rule the pitch should be melted at the lowest temperature, and the solvent in the first instance added in small quantities, after which it may be introduced more freely up to the desired consistency. Rosin, in varying proportions, is occasionally added, but in the majority of cases pitch alone is used. Varnishes, so prepared, will obviously vary in character, drying quality, and lustre, and it is hardly necessary to point out that when required of a nature that shall dry rapidly and with a bright uniform surface both the pitch and the solvent employed should be free from water.

Tar varnishes dry with a bright, hard surface, and adhere both to wood and iron with considerable tenacity. They have been extensively employed for coating the hulls of iron ships as anti-fouling compositions and for the purposes of protective paints generally.

Asphalts and compounds for paving.—Asphalt prepared from substances derived from coal-tar has found a wide application, especially for the purpose of street paving; surfaces of ground coated or covered with asphalt become impenetrable to moisture and the passage of noxious effluvia. Coal-tar asphalt may be regarded as a soft pitch to which body or firmness has been imparted by incorporating sand, grit, gravel, chalk, lime, and substances of a similar character. The soft pitch used for this purpose may consist of the residue from tar after distilling off the more volatile constituents, and known as refined or prepared tar; or it may consist of hard pitch, afterwards melted and thinned down to the required consistency with heavy tar oils, preferably green oils.

The manufacture of this pitch into asphalt suitable for street paving is carried on in various ways. Occasionally the pitch is melted in iron pans and the ingredients to be incorporated simply added and well stirred in the mixture which contains 20–30 p.c. of pitch, and is used while hot and in a plastic condition.

Asphalt, in the form of blocks or slabs, is manufactured for similar purposes, melted pitch being run direct into a pug mill in which it is incorporated with the proper proportion of sand, gravel, or grit, and from this mill the mixture is run direct into sand moulds to harden and solidify.

Tar asphalt is said to be considerably improved by the addition of about 5 p.c. of sulphur, added in small portions at a time during the heating or melting. Much sulphuretted hydrogen is given off, and it is thought that during the heating the sulphur decomposes the constituents rich in hydrogen and thus renders the residue less fusible. Starting with soft pitch or viscid tar, it is said that 75 p.c. may be obtained as a good asphalt, which does not soften in boiling water.

Coal-tar asphalt, or more correctly, very soft pitch, is also employed for constructing 'asphalt pipes.' This industry was introduced by Jaloreau and has been fully described by Behrens (Dingl. poly. J. 208, 377). Endless hemp paper, 7 feet wide, is passed through a semi-cylindrical pan set in a furnace and filled with hot pitch. A roller revolving in the pan takes up the paper saturated with pitch and conveys it to a similar roller forming the core of the pipe, round which any number of layers of paper may be wound. When the desired thickness has been attained, fine sand is dusted on and the cylinder is exposed to considerable pressure. After cooling in water the core is withdrawn and the pipe becomes ready for use. Pipes manufactured in this manner resist very considerable pressure from within. They possess many features of value for special uses and are employed for conveying water, acids, air-blasts for pit ventilation, and for conveying underground telegraph wires.

A tarred or asphalt paper is also manufactured for packing purposes, consisting of wrapping paper impregnated with soft pitch. Another description which has been used for papering damp walls consists of two layers of paper united by a coating of pitch.

A further and more important application of materials, such as paper and felts, saturated with 'prepared or refined tar,' or pitch let down to the required consistency by solution in heavy tar oils, is for the purpose of 'roofing paper or felt.' A considerable quantity of this material is manufactured in Germany and elsewhere.

Owing to the introduction of motor vehicles, the question of reducing the nuisance caused by dust on the roads has become very important and much attention has been directed upon it. It has been found that roads made with soft pitch or prepared tar as a binder not only are less dusty but are more durable and cost less for repairs, maintenance and cleansing. Several patented articles for use as road binding agents have been put on the market, most of which consist essentially of soft pitch. This outlet has an important bearing on the pitch industry, as if a large proportion of the tar produced in the country is used for road making the output of pitch available for briquetting and other purposes will be very materially reduced.

Pitches derived from the distillation of fatty substances.

'*Stearine*' and '*palm pitches*.'—Several pitches of this character are met with in commerce, notably those known as 'stearine,' or 'cotton oil,' 'wool oil,' and 'palm pitch'; the two first-named representing residues from substances consisting mainly of stearic, the third of palmitic acid. Their manner of preparation is as follows:

In the purification of crude cotton-seed oil by caustic soda, a more or less viscid residue is obtained, known as 'foots' or 'mucilage,' which consists largely of stearic acid in the form of an imperfectly formed soap. This material constitutes an article well known in Hull, Liverpool, London, and other centres of cotton-oil refining, which has been extensively dealt with for the recovery of its 'stearine' and pitch. The soapy mucilage thus obtained in the first instance is heated in suitable vessels,

and then gradually decomposed by the addition of dilute sulphuric acid. The treatment separates the 'fatty acids' or 'stearine' in the form of a perfectly black greasy substance, technically known as 'black grease,' which may vary in quantity from a few p.c. to 80 p.c.

The recovery of 'stearine' and stearine pitch follows as a second step in the operation, and consists in submitting the 'black grease' so obtained to a process of distillation by the aid of superheated steam, giving the following yield :—

Inferior oils . . .	6 p.c.
'Stearine'	39 ,,
Pitch	50 ,,
Loss	5 ,,
	100

The pitch thus obtained and constituting the larger portion of the operation, may be 'hard' or 'soft,' varying with the point to which the distillation has been carried. Both are produced and met with in commerce as meeting the requirements of their respective consumers and present the following characters :

Soft stearine pitch, a viscid treacly substance, and hard stearine pitch, a firm, bright, black product, breaking with a well-marked conchoidal fracture. The sp.gr. of this pitch is about 1·35. At 55° it softens sufficiently to twist in the manner referred to under coal-tar pitch, and at 95° to 100° it melts. It is almost completely soluble in benzene and the pyridine bases, but to a much lesser degree in petroleum spirit. To this solvent stearine pitch only gives up about 71 p.c. of its organic matter, 23 p.c. remaining insoluble. Sulphur is present to the extent of 0·04 to 0·06 p.c.

It yields 79 p.c. of volatile organic matter and 21 p.c. of coke, containing 5–6 p.c. of mineral matter or ash. During the operation of heating and burning off a strong, fatty odour is evolved which at once indicates its origin and nature as an oil pitch.

A benzene solution exhibits no bloom or fluorescence, and when examined spectroscopically a cutting out of the blue or violet portions of the spectrum only; no absorption bands are visible. Stearine pitch has been extensively used for the preparation of special black varnishes used in coating tarpaulins, paper, and in various compounds employed for electrical insulation. For these requirements it is eminently adapted from the fact of yielding surfaces and combinations both supple and pliant, and that do not crack and disintegrate in the manner of some mineral pitches.

Wool-oil pitch.—In the scouring and washing of woollen goods, soapy liquors are obtained in considerable quantity. These liquors are now treated for the fatty substances contained in them. The process followed is in many ways analogous to that already described, the fatty acids being separated by heating and addition of dilute sulphuric acid. On submitting these fatty acids to a similar process of distillation, an excellent stearine is recovered with a similar residue of pitch. This pitch may be hard or soft, and in both stages resembles that known as cotton or stearine pitch; it has similar uses and applications. The softer kinds are used as lubricants for heavy machinery under the name of 'hot and cold neck grease.'

Palm-oil pitch.—This pitch, which is now produced in considerable quantity, is the residue of an operation extensively carried out more or less in accordance with an important patent granted to Wilson and Gwynne in the year 1843, in which oils or other fatty substances were heated with sulphuric acid in place of an alkali for separation of their containcd fatty acids.

In the operation claimed, the glycerol is converted into 'sulphoglyceric acid,' which is afterwards washed out, and the resultant black mass distilled with superheated steam. The respective fatty acids pass over in a condition of great purity and suitability for the various purposes applied. With palm oil, palmitic acid distils over, and palm pitch remains in the still.

In appearance and when soft, this pitch varies from those already described. It is dull in colour, with a waxy feel, but when hard is tolerably bright and black in colour, breaking with a distinct conchoidal fracture and small granular surface, but exhibiting the same waxy feel: its sp.gr. varies from 1·045 to 1·050. The softer kind twists at the ordinary temperature; the harder at 30°, although it does not completely melt under 95°. It yields about 80 p.c. of volatile organic matter and 20 p.c. of a light porous coke, containing 6·5 to 6·8 p.c. of ash. During heating a powerful fatty odour is given off, betraying its nature as being also of fatty origin. It is almost wholly soluble in benzenc, but scarcely acted upon by the pyridine bases or petroleum spirit. A solution examined spectroscopically shows a cutting out of the violet portions of the spectrum but no absorption band.

Palm pitch has been extensively used for tarpaulin varnishes, and in combination with paraffin wax, for various electrical insulators. The softer kinds are employed as hot and cold neck greases for heavy machinery.

Bone-oil pitch.—In the dry distillation of bones and other animal substances, an oil is obtained exhibiting a strong fœtid odour and known as bone or 'Dippel's oil' (*oleum animale Dippelii*) (*q.v.*), which when submitted to further distillation yields about 23 p.c. of a hard, firm pitch.

Hard and soft varieties are produced and present the following characteristics: jet black and shining; brittle, and breaking in masses, although distinctly conchoidal; sp.gr. ranges from 1·125 to 1·130. The harder pitches 'twist' at a temperature of 70°, and melt at 98°–100°.

A good sample will yield 63 p.c. of volatile organic matter and 37 p.c. of hard, compact coke, containing from 0·4 to 0·7 p.c. of mineral matter or ash. During the operation of heating and igniting, the characteristic and unmistakable odour of bone or animal oil becomes very powerful and readily distinguishes it from all other pitches. As a solvent, benzene attacks it very imperfectly, but the pyridine bases dissolve it entirely or with the exception of a small quantity of carbonaceous matter. Petroleum spirit dissolves about 30 p.c. Solutions of

this pitch in the pyridine bases exhibit no bloom or fluorescence, and when examined spectroscopically merely a cutting out of the violet portion of the spectrum, no absorption bands being visible. Sulphur is present to the extent of 0·30 p.c.

It exhales a somewhat unpleasant odour, very noticeable when warmed. Its chief uses are for tarpaulin and other varnishes.

Stockholm pitch (*wood-tar pitch*).—Wood-tar, when submitted to distillation, yields distillates of light oils varying in sp.gr. from 0·840 to 0·880 and about 70 p.c. of pitch. In appearance it is jet black and brilliant, but it is inferior to bone pitch. Its fracture is conchoidal, but it is extremely brittle, crumbling between the fingers. It is slightly adhesive and becomes sticky on gently warming. It has a sp.gr. of about 1·105; at 40° it twists easily and at 82° it melts. When heated and ignited it yields 88–88·5 p.c. of volatile matter, leaving a soft, friable coke ranging from 12–11·5 p.c. and containing from 0·7–0·84 p.c. mineral matter or ash. During the burning off, vapours and odours are evolved impossible to mistake for those of any other pitch, or for other than that of wood tar. Benzene dissolves this pitch completely and the pyridine bases equally well; but petroleum spirit only takes up from 91 to 92 p.c., leaving a small portion insoluble. Sulphur is present but in minute quantity only, not exceeding 0·01 p.c.

A solution of Stockholm pitch shows no bloom or fluorescence, and when examined spectroscopically a cutting out of the violet portion of the spectrum only. No bands are visible nor any indication of chrysene, said to exist in this particular tar or pitch.

Stockholm pitch dissolves almost completely in alcohol and potash lye. When its alkaline solution is boiled a coloured oil passes over possessing a stupefying smell, and when acidified and boiled yields volatile fatty acids. A black mass is deposited as the operation proceeds; on boiling this mass with water, creosote is given off. If the acid and alkaline treatment is repeated several times, the mass is converted into a black powder which, after long boiling with hydrochloric acid, yields to alcohol only a small quantity of resin. The black residue insoluble in alcohol and potash consists of—

Carbon	65·04 p.c.
Hydrogen	4·89 ,,
Oxygen	30·07 ,,
	100·00

As wood-tar is a complex mixture of phenoloid bodies, amongst which guaiacol and creosol predominate, and the less volatile fractions contain methyl ethers of pyrogallol and its homologues, it is highly probable that the residual pitch resulting from its distillation at a comparatively low temperature contains amongst its other constituents the methyl ethers of trihydric phenols (*v.* CREOSOTE).

Wood-tar pitch is assumed to possess much of the antiseptic and preservative power of the tar from which it is derived. It finds a considerable outlet for marine purposes and the coating and painting of ships.

Production of wood pitch and tar in Russia.

The production of wood pitch and tar is a highly important industry of the timber districts of Russia. England alone takes over 100,000 barrels yearly of Russian pitch and tar. In normal times pitch is exported chiefly to England from Archangel, where it is one of the principal articles of trade, while turpentine has been shipped to Germany from the Baltic ports and overland. In recent years in western Russia, especially near the Vistula River, large quantities of pitch and turpentine have been distilled from the stumps left after the clearance of woods, this having been in great demand in Germany on account of its good quality and low price. It has been estimated that the Russian forests produce yearly about 124,000,000 lbs. of pure pitch, 62,000,000 lbs. of tar, 5,400,000 lbs. of resin, and 2,160,000 lbs. of turpentine. Up to the present time the methods employed in this industry have been, for the most part, of a primitive character, and carried on in small establishments. Pine wood is almost the only material used, the most resinous parts being the stump and roots. The stumps are allowed to remain 10 or 20 years in the ground before removal, the best parts of the tree being the long vertical roots. In making tar, the method of distillation ordinarily in vogue requires the digging of pits from 10 to 60 feet in diameter, similar to those made for burning charcoal. They are usually dug on the slopes of river-banks. About 20 to 30 feet from the pit an excavation is made in the form of a ditch, the bottom of which is on a lower level than that of the pit. From this excavation a sloping trough is pushed into the centre of the pit, a hole being made in the middle of the latter leading straight into the trough, and in this manner a funnel is made through which the product flows into pails. There is a tendency, however, for improved methods to be adopted. There is a large production of what is called 'polovinchik' (half-pitch), which is used as a dressing for leather, this being the result of distillation of tar mixed with some birch or aspen bark (U.S. Comm. Rept. No. 191, August 16, 1915; J. Soc. Chem. Ind. 1915, 34, 949).

Rosin pitch.—Rosin or colophony, is the residue left on distilling off the volatile oils from crude turpentine, and when submitted to further distillation, yields definite products, but varying considerably with the temperature and conditions of distillation. In a vacuum or current of superheated steam it may be distilled almost unaltered, but when subjected to dry distillation, as in the ordinary method pursued by rosin distillers, it yields a number of products, consisting chiefly of rosin oil, which passes over to the extent of about 85 p.c., including rosin spirit, water, a powerfully anæsthetic gas containing carbon monoxide, ethylene, butylene, pentene, with a residue of pitch amounting to $1\frac{1}{2}$ cwts. from a ton of rosin.

Rosin pitch is a yellowish-brown substance, hard and compact but easily crumbling on slight pressure. It has a sticky feel, and when warmed exhibits the characteristic odour of resin. Its sp.gr. varies from 1·090 to 1·095; at a temperature of 35° it twists readily, and at 68° melts. When heated and ignited it yields

82·5 p.c. of volatile matter, leaving a spongy soft coke amounting to 17·5 p.c., which contains 0·58 to 0·7 p.c. of mineral matter or ash. During the heating a strong odour of rosin is given off, readily distinguishing it from Stockholm or wood-tar pitch. In benzene and the pyridine bases it is completely soluble, but petroleum spirit only takes up 86·94 p.c., leaving 13·06 p.c. insoluble: sulphur is present to the extent of 0·26–0·3 p.c.

Solutions of rosin pitch exhibit a deep greenish bloom or fluorescence, but differing from that of coal-tar pitch, which is invariably yellow. Spectroscopically, they merely show a cutting out of the blue and violet portions of the spectrum; absorption bands are absent.

Rosin pitch finds no special use by itself, but is occasionally mixed with other pitches of an inferior description.

Ozokerite and ceresin pitch are obtained from the distillation of crude ozokerite, and the following figures have been furnished by E. J. Mills as representative of the operation:—

Very light oils	20
Heavy oils	50
Paraffin	8
Hard pitch	8
Loss	14
	100

B. Redwood (J. Soc. Arts, 34, 886) gives the products of Galician ozokerite as 5 p.c. of gaseous hydrocarbons, 3 p.c. of naphtha, 6 p.c. of semi-solid 'ozokerine,' 12 p.c. of soft paraffin (melting at 44°–46°), distilled ozokerite (melting at 61°), and black waxy residue. It is a hard, waxy substance breaking with a rough granular surface and irregular fracture. Its colour is dark amber, inclining to brown; its sp.gr. is 0·950. At a temperature of 50° it twists, and at 85° melts; heated and ignited it yields 9·7 p.c. of volatile organic matter, leaving 3 p.c. of soft, friable coke containing traces only of mineral matter or ash. During this operation the odour evolved is simply that of highly-heated paraffin. It is completely soluble in benzene but not wholly so in the pyridine bases, the solution showing no bloom or fluorescence. Examined spectroscopically, no absorption bands are visible, but a cutting out of the blue and violet portions of the spectrum only, as is the case of the pitches already described.

Ozokerite and ozokerite pitch have been found to possess remarkable electrical qualities, and in admixture with various substances, caoutchouc among them, have formed the subject matter of several patents. Such compounds have found extensive uses for coating telegraph wires and for insulating purposes generally.

Petroleum pitch.—In the first distillation of crude petroleum oil, the charges may be run down to a coking point or they may be discontinued at a stage at which pitch or artificial asphaltum would result on cooling.

Large quantities of oil pitch are made from Texas, Californian, and Mexican oil, and in Europe from Galician and Rumanian oil, and are used to a considerable extent, especially in America, for architectural, road making, insulating and general waterproofing purposes, and as anti-corrosive paints or coatings for steel work (Mansbridge).

In appearance it greatly resembles natural bitumen or asphaltum; it is jet black and shining, and breaks with a similar conchoidal fracture. It has a sp.gr. of about 1·120. At a temperature of 45° it 'twists,' at 84°–85° melts; heated and finally ignited it yields about half its weight of volatile organic matter. The odour evolved is characteristic of petroleum, but differs entirely from that of natural asphaltums, with which it cannot be confounded. Mineral matter is present in minute traces only. Benzene dissolves this pitch completely, affording a solution exhibiting a strong yellow bloom or fluorescence not unlike that observed with coal-tar pitch. It is, however, almost insoluble in the pyridine bases; petroleum spirit dissolves 36·16 p.c. only. The residues from American petroleum contain notable quantities of closed chain hydrocarbons, among which anthracene, phenanthrene, chrysene, chrysogen, and pyrene have been recognised, as also a hydrocarbon called thallene. From Californian petroleum the hydrocarbon picene $C_{22}H_{14}$ has been isolated. When treated with sulphuric acid, it yields a sulphonic acid dissolving in water with a splendid blue-green fluorescence. Petroleum pitch, although differing in its physical aspect, may, in many respects, be looked upon as resembling coal-tar pitch.

B. Poro (Gazz. chim. ital. 13, 77) gives the following figures as showing the results of distilling Italian petroleum:—

	I.	II.
Oil	63·5	66·9
Pitch	32·2	28·3

Petroleum pitch has been used in compounding cements, asphalts, varnishes, and patent fuels.

Shale-oil pitch is now quite unknown, manufacturers of shale oil preferring to continue its distillation to the extent of coking.

Bibliography.—Lunge's Coal Tar and Ammonia (4th edit.), 1909; Allen, Commercial Organic Analysis (2nd edit.), 1886; E. J. Mills, Destructive Distillation; S. F. Peckham (Amer. J. Sci. [iii.] 28, 105–117); Stripplemann and Engler (Dingl. poly. J. 250, 216, 227, 271, 316, 321); Boussingault (Compt. rend, 96, 1452, 1456); B. Delachanal (*ibid.* 97, 491, 494); S. Bernus (Bull. Soc. chim. de Belgique, 1911, 7); Mansbridge (J. Soc. Chem. Ind. 1918, 182 T); H. Abraham, Asphalts and Allied Substances, 1919.

PITCHBLENDE, or **Uraninite** (Ger. *Uranpecherz*). A uranium mineral which is much sought for as an ore of radium. Its occurrence in the ancient silver-mines at Joachimsthal in Bohemia was known as early as 1727; and it was in this mineral that M. H. Klaproth discovered in 1789 the element uranium. The old German names Pecherz, Pechblende, &c., were suggested to the miners by a superficial resemblance of the mineral to pitch and to zinc-blende. The name Uranin, proposed by W. Haidinger in 1845 and later modified by Dana into Uraninite, is sometimes used in a rather wider sense to include the massive variety (pitchblende) and the crystallised varieties ('uranoniobite,' cleveite, bröggerite, and nivenite).

The mineral, although possessing certain points of considerable interest and a high value, is unattractive in appearance. It is opaque and black with a dull pitchy lustre (crystals are brighter and with a sub-metallic lustre) and breaks with a sub-conchoidal to uneven fracture. The streak, or colour of the powder, is brownish- or greenish-black. The only feature that attracts attention is the remarkably high density (sp.gr. 6·4–9·7). This feature serves to distinguish the mineral from the more commonly occurring chromite; in its non-magnetic character it differs from magnetite; and in the absence of cleavage from wolframite—these being minerals often mistaken by prospectors for pitchblende. From some other heavy black minerals, such as columbite and tantalite, the distinction is less easy in the absence of chemical tests. Pitchblende can, however, always be quickly and readily recognised by means of its radio-active character; and without the aid of such simple and portable instruments as the spinthariscope (or scintilloscope) and gold-leaf electroscope the chances of the prospector are small. Although actively sought for since the discovery of radium in 1898, it is a remarkable fact that no new deposits of pitchblende of any importance have been brought to light.

Two distinct varieties, with very different modes of occurrence, are known. One is met with in a massive form, sometimes showing a mamillated or botryoidal surface, in mineral-veins together with ores of silver, lead, copper, or tin, and frequently associated with ores of nickel, cobalt, and bismuth. The other variety is found as small (1–3 cm. across) octahedral or cubo-octahedral crystals in pegmatite-veins traversing granitic rocks. These two varieties differ somewhat in chemical composition and in sp.gr. (6·4–8 for the massive, and 7·5–9·7 for the crystallised variety).

The mineral has been variously regarded as an oxide of uranium or as a uranate of uranyl, lead, thorium, &c. In composition it is subject to wide variations. The principal constituents are uranous and uranic oxides, but these are present in varying relative proportions. Lead is also invariably present, but it is only the crystallised varieties that contain in addition thorium and metals of the cerium and yttrium groups. Some of the many constituents shown in the analyses are no doubt present as mechanically admixed impurities, this applying more particularly to the massive variety of lower specific gravity. Thus an analysis by F. Janda (Oesterr. Zeitsch. Berg- u. Huttenw., 1902, 1, 283; abstr. Chem. Zentr. 1902, ii. 150) of an average sample of the Joachimsthal ore gave: U_3O_8, 49·95; As_2S_3, 0·71; PbS, 1·85; PbO, 0·25; Cu_2S, 1·12; Bi_2S_3, 0·31; Ag_2S, 0·04; FeS_2, 7·93; Fe_2O_3, 1·14; $FeCO_3$, 6·96; Al_2O_3, 3·25; ZnO, 1·09; MnO_2, 0·11; $CaCO_3$, 3·69; $CaSO_4$, 0·89; $MgCO_3$, 0·76; $MgSO_4$, 0·07; SiO_2, 18·55; V_2O_5, 0·02; H_2O, Na_2O, K_2O, P_2O_5, 1·34; $PbSO_4$, $CuSO_4$, Ni, Mo, W, Ra, traces.

Several (22) detailed analyses have been made by W. F. Hillebrand, but he failed to arrive at a definite formula for the mineral (Amer. J. Sci. 1890, 40, 380; Bull. U.S. Geol. Survey, 1891, No. 78; 1892, No. 90; 1910, No. 419). The following analyses, I–V, are by Hillebrand. I, bright crystals from Branchville, Connecticut. II, massive from Johanngeorgenstadt, Saxony; III, massive from Gilpin Co., Colorado; IV, crystals ('bröggerite') from Ånneröd, Norway; V, crystals ('cleveite') from Arendal, Norway; VI, (W. Marckwald, Centr. Min. 1906, 761), crystals from Lukwengule, Uluguru mountains, East Africa.

	I.	II.[1]	III.[2]	IV.	V.	VI.
UO_2	72·25	59·30	58·51	46·13	24·18	87·8
UO_3	13·27	22·33	25·26	30·63	41·71	
ZrO_2	7·20	nil	7·59	0·06	3·66	—
ThO_2		nil	—	6·00		—
CeO_2	—	nil	0·22	0·18		—
$(La,Di)_2O_3$	—	nil	—	0·27		—
$(Y,Er)_2O_3$	—	nil	—	1·11	9·76	—
PbO	4·35	6·39	0·70	9·04	10·54	7·5
FeO	—	—	0·32	—	—	1·0
Fe_2O_3	0·11	0·21	—	0·25	0·03	—
MnO	0·10	0·09	0·16	—	—	—
CaO	0·18	1·00	0·84	0·37	1·06	2·1
MgO	—	0·17	tr.?	tr.	0·10	—
Alkalis	—	0·31	tr.?	tr.	0·23	—
H_2O	0·68	3·17	1·96	0·74	1·23	0·5
He, &c.	n.d.	tr.	0·02	0·17	n.d.	—
SiO_2	0·03	0·50	2·79	0·22	0·90	0·3
P_2O_5	—	0·06	0·22	0·02	—	—
Insol.	0·04	—	—	4·42	1·10	0·2
	98·21	97·93	99·82	99·61	94·50	99·4
Sp.gr.	9·733	6·89	8·068	8·893	7·50	8·84

In the least altered specimens uranium dioxide (UO_2) predominates, whilst in those showing signs of alteration there is more uranic oxide (UO_3) and water. The latter pass into the alteration-product known as gummite (*q.v.*), which contains mainly uranic oxide together with much water. Since the dioxides of uranium, thorium, and cerium have been obtained artificially as cubic crystals, it seems probable that uraninite may be regarded as an isomorphous mixture of these oxides, the formula then being (U, Th, Ce, Pb)O_2. This view is supported by the discovery of the closely allied cubic mineral thorianite (*q.v.*), in which thorium oxide predominates over uranium oxide.

Containing a higher percentage of uranium than any other mineral, pitchblende is correspondingly richer in radium, but this amounts to only one part in five million (*i.e.* about 200 mg. per ton). About 0·1 gram of radium chloride can be extracted from a ton of ore containing 50 p.c. U_3O_8. On the process of extraction employed at the Joachimsthal works, *see* L. Haitinger and K. Ulrich, Sitz.-ber. Akad. Wiss. Wien, 1908, 117, [iiA], 619. The inert gas liberated from pitchblende when the mineral is dissolved in acid or when heated *in vacuo* was first detected by W. F. Hillebrand in 1890, and believed by him to be nitrogen. This led Sir W. Ramsay in 1895 to the discovery in this mineral of terrestrial helium. Argon is also present.

By its alteration in nature pitchblende gives rise to a number of secondary uranium minerals. These are yellow in colour, and are often to be

[1] Anal. II includes also: Al_2O_3 ?, 0·20; Bi_2O_3, 0·75; CuO, 0·17; As_2O_5, 2·34; V_2O_5, MoO_3, WO_3, 0·75; SO_3, 0·19.

[2] Anal. III includes also: As_2O_5, 0·43; $CuFeS_2$, 0·12; FeS_2, 0·24; ZnO, 0·44; TiO_2, trace.

seen as an earthy coating on the surface of hand-specimens of pitchblende: when met with in the upper oxidised zones of mineral veins, they form a valuable indication of the presence of the mineral. By simple oxidation and hydration it passes into gummite—a heavy, reddish-yellow mineral with a gummy appearance. In the presence of sulphuric and carbonic acids (the former produced by the weathering of iron-pyrites commonly associated with pitchblende), it alters to a number of hydrated and basic uranium sulphates and carbonates—the so-called uranium-ochres (johannite, liebigite, *q.v.*, &c.). In the presence of phosphatic solutions it gives the so-called uranium-micas (autunite, *q.v.*, torbernite, &c.).

The localities at which pitchblende has been found are relatively few in number, and it is only in three districts that the mineral has been found in quantities sufficient for mining. These are in the mineral-veins of Cornwall, of the Erzgebirge on the borders of Saxony and Bohemia, and in Gilpin Co., Colorado.

In Cornwall, the workable deposits are those of the South Terras mine in the parish of St. Stephen-in-Brannel near Grampound Road, and the Trenwith mine at St. Ives. The occurrence of pitchblende has, however, been recorded in some 25 other Cornish mines in the parishes of St. Just-in-Penwith, St. Ives, Penzance, Gwinear, Camborne, Illogan, Redruth, Gwennap, Wendron, St. Gluvias, Perranarworthal, St. Stephen-in-Brannel, and Lanivet. In Devonshire, at the Kingswood mine near Buckfastleigh. On the Saxon side of the Erzgebirge it has been found at Johanngeorgenstadt, Schneeberg, Annaberg, Marienberg, Freiberg, Breitenbrunn, Schwarzenberg, and Gottesberg; and on the Bohemian side at Joachimsthal (= Jáchymov) and Schlaggenwald (= Slavkov). (On the mode of occurrence at Joachimsthal, *see* J. Stěp and F. Becke, Sitz.-ber. Akad. Wiss. Wien, 1904, 113, [i], 585.) Other European occurrences are in the mineral-veins of Przibram in central Bohemia, and Rezbanya in Hungary. A specimen has also been described from near Adrianople in Turkey (J. L. Smith, 1848). Near Central City in Gilpin Co., Colorado, pitchblende is worked on the Wood and Kirk lodes. It occurs, apparently in some abundance, with copper-ores in the Kasolo and Luiswishi mines in Katanga, Belgian Congo. A specimen of doubtful origin has been described from New South Wales (T. H. Laby, 1909). The localities above mentioned all refer to the occurrence of massive pitchblende in mineral veins.

The crystallised varieties occur as small crystals sparsely scattered in pegmatite veins, and are occasionally met with as isolated specimens in the felspar quarries in the south of Norway, at several places in the neighbourhood of Moss (Karlshus, Raade, Ånneröd, Elvestad, Huggenäskilen, Skraatorp), near Arendal (Garta quarry and Tvedestrand), and in Sætersdalen (Evje). In the United States, crystals have been found in the felspar quarries at Middletown, Glastonbury, and Branchville in Connecticut. In the Flat Rock mine and other mica mines in Mitchell Co., and Yancey Co. in North Carolina. At Marietta in South Carolina; Barringer Hill in Llano Co., Texas; and rather abundantly in the Bald mountain district in the Black Hills of South Dakota. Canadian occurrences are in mica mines at Villeneuve, Ottawa Co., Quebec, and in Butt township, Ontario. Crystals have also been found in a mica mine at Lukwengule in the Uluguru mountains, Tanganyika Territory, East Africa. As crystals and large nodules it is found in the mica mines at Singar, Pichhli, and Abraki Pahar, in the Gaya district, Bengal. Other recorded localities are in Ceylon, Borneo, and Colombia (South America).

Curiously, this ore, now of such great value, was a source of embarrassment to the earlier miners, and it was thrown aside as worthless. Some of the old waste heaps are now being worked over for pitchblende. Since about 1830, it has been used for the extraction of uranium oxides, and in 1853 works were established by the Austrian Government for this purpose at Joachimsthal in Bohemia. The oxides were used in producing rich velvet-black, yellow, and orange colours in porcelain and enamels, and in the manufacture of the well-known fluorescent uranium glass. Limited amounts of the ore have also been used for the preparation of uranium salts employed as chemical reagents and in photography. A more recent application of uranium is in the manufacture of steel for guns.

The limited and uncertain nature of the deposits is well illustrated by the variations in the output of the pitchblende ore. In 1890, Cornwall and Bohemia produced 22 and 25 tons, and in 1897, 30 and 44 tons respectively. After the discovery of radium, the output increased to a maximum of 103 tons in 1905 in Cornwall, and of 52 tons in 1900 in Bohemia. Since then it has decreased to 6 and 8 tons respectively in 1909. Saxony produced only $\frac{1}{3}$ ton in 1909. In Colorado, the output of pitchblende has varied between 4 and 20 tons per annum.

L. J. S.

PITCHSTONE (Ger. *Pechstein*). A glassy igneous rock with the same chemical composition as granite, quartz-porphyry, rhyolite, and obsidian (SiO_2 about 73 p.c.), but containing much more water (5·5–11 p.c.). It has a characteristic dull, resinous or pitchy lustre and conchoidal fracture. The colour is usually dark green to black, or sometimes brown or reddish; sp.gr. 2·2–2·4. Porphyritic crystals of felspar and quartz are sometimes embedded in the glassy material; and the glass is usually crowded with microscopic skeletal crystals of great beauty. These rocks are found as thin dykes and sheets, and have been formed by the rapid cooling of an acid magma rich in water injected along fissures of pre-existing rocks, the pressure being sufficient to keep the water imprisoned. When the rock is artificially fused it blows up into pumice. Well-known occurrences of pitchstone are at Meissen in Saxony and on the islands of Arran and Eigg in Scotland.

L. J. S.

PITTACAL *v.* EUPITTONIC ACID; TRIPHENYLMETHANE COLOURING MATTERS; WOOD, DISTILLATION OF.

PITTOSPORUM UNDULATUM (*Vent.*). The fruit of this tree which is indigenous to South-Eastern Australia, where it is known as 'mock-orange,' yields by distillation an oil of an orange-like odour and contains a large proportion of *limonene* besides small amounts of *pinene* and

various esters and an optically inactive *sesquiterpene* (Power and Tutin, Chem. Soc. Trans. 1906, 89, 1083).

PITUGLANDOL *v.* Pituitary Body.

PITUITARY BODY (*Hypophysis cerebri. Hypophyse*, Fr., Ger.). Oliver and Schäfer (J. Physiol. 1895, 18, 277) showed that extracts of the pituitary body or *hypophysis cerebri* (a small appendage at the base of the brain) have the power of raising the blood pressure on intravenous injection. The pressor principle is only contained in the posterior or infundibular portion. Pituitary extracts also cause a greatly increased flow of urine (Schäfer and Herring, Phil. Trans. 1906, 199 B, 1), and of milk (Ott and Scott, Therap. Gazette, 1911, 35, 689; Schäfer and Mackenzie, Proc. Roy. Soc. 1911, 84, 16). Therapeutically the most important effect of pituitary is, however, a powerful contraction of the uterus, discovered by Dale (Bio-Chem. J. 1909, 4, 427; *cf.* also von Frankl-Hochwart and Fröhlich, Arch. exp. Path. Pharm. 1910, 63, 347). This action was first applied clinically by Bell (Brit. Med. J. 1909, ii. 1609), and the great value of pituitary as a uterine stimulant has since been confirmed by numerous clinicians. This led to various attempts to isolate the pure acetine principle, which have so far all failed. Comparatively pure extracts may be prepared by dissecting out the infundibular portion of fresh glands (generally of the ox), grinding with sand, boiling with water acidulated with acetic acid, and filtering. Clear and colourless extracts of this kind are on the market under various names (Hypophysin, Pituitrin, Pituglandol, Coluitrin).

An extract so prepared contains little protein and some phosphates. The latter may be quantitatively precipitated by uranyl acetate, when most of the protein is also carried down; the filtrate remains active. Almost the only precipitant of the active principle is phosphotungstic acid; this principle is therefore possibly a base. Führer (Zeit. f.d. ges. exp. Medizin, 1913, 1, 397; Deutsch. med. Wochenschr. 1913, 39, 491) states that the Farbw. vorm. Meister Lucius and Brüning (D. R. P. 268841, 1912) have obtained no less than four crystalline sulphates, all physiologically active, but it seems almost certain that these were all contaminated with the active principle. The isolation of the active principle has also been claimed by Baudouin (C. R. Soc. de Biol. 1913, 75, 1138) and by Bouin and Ancel (*ibid.* 1914, 76, 62, 110), and by F. Hoffmann-La Roche & Co. (D. R. PP. 282002, 1913, and 284148, 1913). According to the latter patents the glands are extracted with aqueous sodium carbonate, and the solution is washed with chloroform, which removes a substance acting on the intestine. The substance acting on blood pressure and uterus is removed from the residue, after neutralisation with hydrochloric acid, as the hydrochloride, which is obtained crystalline by the addition of ether to its alcoholic solution. According to Abel and Pincoffs (Proc. Nat. Acad. Sci. 1917, 3, 507), however, 'hypophysin' is a mixture of albumoses and peptones with varying and unknown amounts of active and inactive constituents of the gland. There has been considerable speculation as to a possible relationship of the principle acting on the uterus to β-iminazolylethylamine, which acts somewhat similarly (*see* Ergot). Thus the crystals obtained by Meister Lucius and Brüning gave Pauly's histidine reaction, characteristic of the ergot base, and Aldrich (J. Amer. Chem. Soc. 1915, 37, 203) obtained the same reaction with extracts (but compare Pauly, Zeitsch. physiol. Chem. 1915, 94, 426). The main chemical facts known about the pituitary active principle are that it is very readily destroyed by alkali and also by trypsin (Dale, Bio-Chem. J. 1909, 4, 427). The latter property seems to indicate a peptide structure, and led Guggenheim (Biochem. Zeitsch. 1913, 51, 369) to synthesise peptides of β-iminazolylethylamine ('peptamines'), which were, however, only slightly active. The great susceptibility to alkali is shared by acetylcholine (*see* Ergot), and has led to speculations that the active principle might be an acetyl alkanolamine (Guggenheim, Biochem. Zeitsch. 1917, 81, 274; Führer, *ibid.* 1916, 76, 232). *See* for later attempts at isolation, Abel and Nagayama, J. Pharm. exp. Therap. 1920, 15, 347; Dale and Dudley, *ibid.* 1921, 18, 27; Abel and Rouiller, *ibid.* 1922, 20, 65.

Hypophysis sicca, U.S. P., is the posterior lobe of the pituitary body of cattle, cleaned, dried and powdered. *Liquor hypophysis* is also official in the U.S. P. The B. P. has not yet admitted pituitary preparations. The activity of extracts can only be determined by physiological test (blood pressure, isolated uterus). An interesting new method utilises the contraction of the melanophores of a minnow (Spaeth, J. Pharm. exp. Therap. 1918, 11, 209; *cf.* Hogben and Winton, Bio-Chem. J. 1922, 16, 619).

Disturbance of the pituitary body is associated with the rare disease acromegaly, characterised by an enlargement of the bones of the lower jaw, hands, and feet. Brailsford Robertson (J. Biol. Chem. 1916, 24, 409) has extracted from the anterior portion of the pituitary a phosphalide, *tethelin*, for which he claims that it has a definite effect on the growth of mice, but compare Drummond and Cannan (Bio-Chem. J. 1922, 16, 53), who deny this. G. B.

PITUITRIN *v.* Pituitary Body.

PITURI. The leaves of *Duboisia Hopwoodii* (F. v. Müll.), used as a narcotic (Brestowski, Handwörterbuch Pharm. 370). On distillation with steam was stated to yield an alkaloid, a colourless oil, b.p 243°, called *piturine*. Rothera has shown, however, that the only alkaloid present is nicotine, which forms 2·67 p.c. of the leaves after drying at 60° (Bio-Chem. J. 1910, 5, 193).

PIURI *v.* Indian yellow.

PLAGIOCLASE *v.* Felspar.

PLANCHEITE *v.* Dioptase.

PLANT-SPRAYS. Spraying may be taken in a wide sense to embrace the application of solids, liquids, or gases to plants, with the object of freeing them from insect or fungoid parasites, or of cleansing them from dead bark, and such adventitious deposit or growth as interferes with the healthy functions of the plant.

Solids.

Many liquid spray-fluids, or washes, contain solids in suspension, but it is only in a few cases that solids are used in the dry state;

in such cases they are blown on to the plants by means of bellows, and the operation must be performed while the plants are wet with dew or mist, so that the solid may adhere to them. *Sulphur*, in the form of flowers of sulphur, is applied extensively in this way to hops for destroying mildew and red spider, and in certain other cases it is applied mixed with *lime*. The nature of its action is at present obscure, but most probably depends on its being slightly volatile, for, when used in hot-houses, the most satisfactory results are obtained when it is painted on to the hot-water pipes, or otherwise heated. At the same time its effectiveness is increased by the presence of moisture, though it hardly seems possible that the traces of sulphuric acid formed under such conditions can account for its action. Hellebore, consisting of the root-stock and roots of *Veratrum album* (Linn.) and *V. viride* (Ait.) is effective in destroying caterpillars on gooseberries, &c.: it acts chiefly by poisoning their food, but is probably also injurious to them by contact with their bodies. As it is less poisonous than arsenical compounds, and loses its properties rapidly on exposure to air, it may be used with safety within a short time of the ripening of the fruit. Pyrethrum, obtained from the ground heads and stems of *Chrysanthemum* [*Pyrethrum*] *roseum* (Web. et Mohr) and *C. Marschallii* (Aschers.), and *C.* (*Pyrethrum*) *cinerariæfolium* [(Trav.) Bocc.], contains an oil which appears to act on insects only by contact. Besides being used in the dry form, it is used as a decoction and also as a fumigant.

Liquids.

A. Insecticides. For a determination of the nature of the insecticide which is likely to be effective in any particular case, a knowledge of the life-history of the insect is necessary, to indicate at what period it is most vulnerable, and by what means it may best be combated. Insects which chew the leaves are best dealt with by poisoning their food, whilst others which pierce the leaves and bark, extracting the juices from below the surface, are best attacked by the application of some corrosive substance to their bodies. The most effective procedure, where practicable, is to destroy the eggs of the insect: for this, a corrosive substance is required, and such can only be applied to the plants while these are in the dormant condition. For facilitating insect eggs being reached by a fluid, as well as for reducing the number of crevices in which insects can deposit their eggs, the application of a detergent wash in the winter, to remove dead bark, moss, lichen, &c., from the trees, is an important adjunct to an insecticide.

Many of the most popular insecticides and fungicides have come into use by accident, and although practical experiments have introduced considerable improvements in them, much uncertainty still prevails as to the method of their action; and it is remarkable that in very few cases has science provided satisfactory substitutes for these chance selections.

The chief classes of insecticides are (1) vegetable poisons consisting of alkaloids, (2) soft soap, with or without excess of alkali, (3) sulphur and sulphides, (4) phenol, (5) paraffin oil, (6) arsenical compounds, (7) lime.

(1) Of the vegetable poisons, *hellebore* and *pyrethrum* have already been mentioned, and these may be sprayed on to the trees in the form of a 3 or 4 p.c. admixture with water or dilute paraffin oil emulsion. If a decoction is used it should not be boiled. *Quassia* with soft soap is much used for destroying aphis. The wash is made by boiling ½ to 3 lbs. of chips of the wood with 10 gallons of water, and adding ½ to 3 lbs. of soft soap.

Nicotine appears to be by far the most effective of the vegetable insecticides. A decoction of 'denatured' tobacco—which contains about 70 p.c. of tobacco mixed with sulphur, asafœtida and flour—may be used, but owing to the great variation in the nicotine-contents of tobacco, it is better to use nicotine itself. A solution of 0·075 p.c. strength is very effective for aphis, apple psylla, &c.: it is well to add to the solution 0·5 p.c. of soft soap.

It is noticeable that various alkaloids, such as aconite, hyoscyamine, nux vomica, &c., which are highly poisonous to vertebrate animals, have but little action on insects.

(2) *Soap* is generally used in connection with other substances, as in the instances just mentioned, but it is also used effectively alone for killing certain aphides such as those attacking roses. It is probable that its action in such cases is due to its clogging the breathing apparatus of the insect: its low surface tension also enables it to wet bodies more effectively than other spray-fluids, though it may be remarked, a similar action in the case of saponin does not appear to increase the effectiveness of substances to which it is added. Soap is also largely used as an agent for emulsifying paraffin oil. In connection with this, and especially if alkali is added as well, it is used for the destruction of insect eggs, although its chief function under such circumstances is that of a detergent.

(3) *Sulphur* is generally used in the solid condition, as mentioned above, although it occasionally is made into a liquid wash with water and other substances. As an insecticide, and still more as a fungicide, the *sulphides* play an important part. The origin of their use seems to have been the application to trees of a liquid used as a sheep dip, and known as the lime-sulphur-salt wash (California wash) or the lime-sulphur-soda-salt wash (Oregon wash). There are many recipes for making these, the more usual being to boil together for 45 minutes 3 to 6 lbs. of quicklime with 3 lbs. of sulphur, 3 lbs. of salt, and a limited quantity of water, the resulting liquid being afterwards diluted to 10 gallons. In the Oregon wash, about 1 lb. of caustic soda is added, in addition to the above materials, and the heat generated on adding water to the mixture is sufficient to obviate the application of external heat. A wash of this strength can be used only on dormant trees, and is then more effective when applied hot; but at a lesser strength it is now being used on trees in leaf, chiefly as a fungicide. The wash always contains a considerable proportion of unaltered lime, the sulphur going into solution as calcium thiosulphate and pentasulphide. The latter undergoes rapid change even in

absence of air, the pentasulphide becoming converted into thiosulphate with the liberation of sulphur, and the thiosulphate into sulphite and more free sulphur: the sulphite ultimately oxidises to sulphate. Where caustic soda is used in its preparation, the sulphur reacts with it in preference to the lime. The method of operation of this wash is uncertain. It is used habitually in the Western States of America for combating San José scale, and according to certain experiments, none of the substances which it contains, when used separately, have any effect on the scale: according to other authorities, a mixture of potassium sulphide and lime is as effective as the wash. It appears that its action is in part mechanical, the sulphur deposited from it on to the trees glueing the scales to the bark, and preventing the egress of the young insects. What function the salt performs is obscure, and according to some investigators it may be omitted without detriment. Owing to the excess of lime present in it, and to the destructive action of sulphides on lichen, &c., the wash is a good detergent.

Lime and sulphur mixed with water without heating are sometimes used for aphis, mites, and red spider, being preferable to sulphur by itself; such a mixture always contains some products of the reaction of the two substances. Calcium sulphide solution is also used for the same purpose, but potassium sulphide is preferable, as soft soap can be added to it without causing decomposition: 3 to 10 ozs. in 10 gallons are the proportions recommended. It can also be mixed with an emulsion of paraffin oil.

(4) *Phenol*, either dissolved by itself in water, or with the addition of soap or glycerol, has been tried as a general insecticide without much success, but a solution of carbolic acid soap is very effective for certain aphides as well as mildews (*e.g.* of roses), and phenol figures as one of the ingredients of several proprietary insecticides which are now in use.

(5) *Paraffin oil* was used for spraying purposes very soon after it was first obtained. The undiluted oil cannot be used on trees, even in the dormant season, without some risk of injury, but injury does not always follow, even when the trees are in leaf, and it is a very satisfactory remedy to apply in cases (*e.g.* woolly aphis) where the eradication of a pest from a plantation is of more importance than the possible injury to some of the trees. In that case, a pneumatic sprayer should be used, which distributes the liquid in the form of a very fine mist. A good quality lighting oil must be used, higher boiling oils are certain to injure the trees, and so do the more volatile oils (petrol), due, probably, in the latter case to the cold produced by evaporation. Mixtures of oil and water, unless quite dilute, appear to do more damage than undiluted oils. The admixture of oil with water used to be effected by pumping the liquids from separate containers into one delivery hose fitted with a spraying nozzle. It is now more general to emulsify the oil in the water either by means of soft soap or of certain finely divided solids, such as the basic sulphates of iron or copper, obtained by precipitating the normal sulphates with lime-water or milk of lime. For plants in leaf, the proportion of oil should not exceed $1\frac{1}{2}$ p.c., but where they are dormant 6 or 7 p.c. may safely be used. Much larger proportions are often used in America. For dormant trees it is usual to add to the emulsion $2\frac{1}{4}$ p.c. of caustic soda, which makes the wash a powerful detergent, as well as an insecticide as regards the eggs of certain insects. In that case, a basic sulphate should be used instead of soap as the emulsifying agent, although there are special brands of soap which act fairly well under the circumstances; those containing a large proportion of stearate yield a sufficient supply of small insoluble particles to prevent total de-emulsification when the potash soap is flocculated by adding the soda. Emulsions of paraffin may be used in conjunction with most insecticides and fungicides.

(6) *Arsenical compounds.* These supply some of the most powerful insecticides for leaf-eating insects. An aceto-arsenite of copper (Paris green), made by the action of arsenious oxide on verdigris, was one of the first of these substances to come into use, but it is liable to injure the foliage, the leaves becoming scorched, and often falling. This action is intensified if the Paris green contains excess of arsenious oxide, as it often does, and it is well to guard against this by the addition to it of an equal weight of lime. Calcium arsenite, made by boiling arsenious oxide with lime, is also used, although more frequently in the form of London purple, which is a waste product from dye-works, and contains 75 p.c. of the arsenite. The compound which has come most into favour of recent years, chiefly on account of its causing very little leaf-scorching, is lead arsenate, also called gypsine, from its being first used for the gipsy moth caterpillar. When prepared by the precipitation of lead acetate by sodium arsenate (7 oz. of the acetate to $3\frac{1}{2}$ oz. of the crystallized, or to 2 oz. of the 'dry' arsenate for every 10 gallons) it consists of the triplumbic salt, $Pb_3(AsO_4)_2$, but when lead nitrate is used, the product consists chiefly of $Pb_2H_2(AsO_4)_2$. Both substances are slightly soluble, the latter being the more soluble of the two, and they are in a fine state of division which facilitates their distribution over, and adherence to, the leaves. The insecticide is sold in the form of a paste, mixed sometimes with other materials, and is preferable to the home-made material, inasmuch as it is free from the small proportion of acetic acid liberated in the reaction, which tends to cause leaf-scorching.

Acid lead arsenate is said to be more effective than the basic salt. To adhere effectively when sprayed the particles must be as small as possible. The addition of a small quantity of gum arabic is of advantage.

(7) *Lime* has been used of late years together with salt, as an insecticide in special cases (apple psylla). The lime-salt wash is made by slaking 15–20 lbs. of lime, adding 2–3 lbs. of salt, $\frac{1}{2}$–1 lb. of water-glass, and making up to 10 gallons. It is applied to the trees, as hot as possible, a few weeks before the buds open. The wash appears to act partially by destroying the eggs and partially by glueing them up and preventing the egress of the insects. What function the salt performs it is difficult to see. Strong brine will destroy insect eggs by depleting them of their liquid contents, but the

proportion of salt present in this wash is hardly sufficient for such an action.

B. **Fungicides.** Sulphur, and the sulphides previously described, are important fungicides, the latter being of special use in the case of surface moulds or mildews. Phenol and the salts of iron appear to have but very feeble fungicidal properties, and mercuric chloride, although of great value in the laboratory, has not been successfully applied to plants. By far the most important fungicide appears at present to be copper, and it has been applied in a great variety of forms.

The problems of fungicidal action are complex and, at present, very obscure. A fungus destroys its host-plant by the development of mycelium, or thread-like roots, which penetrate and break up the plant cells. As these do their work within the body of the plant, they cannot be reached by any fungicide. Remedial measures must depend on killing the spores or seeds of the fungus, or else on protecting the plant in such a way that fungus spores alighting on it will find conditions unsuitable for germination. A fungus being, like its host, a plant, anything deleterious to it is likely to be deleterious to the host-plant also, and a scorching action on foliage has been found to be a general concomitant of fungicidal action, although under certain weather conditions such damage does not take place. When a plant is in the dormant condition, and a strong fungicide can be used on it, the fungus also exists in the form of resting spores which are very resistive to treatment.

For a substance to be operative, it must either be soluble to start with or become soluble during use. The insoluble copper compounds used as fungicides apparently become soluble by the agency of carbon dioxide, copper sulphate being the substance liberated; and the evidence at present seems to be against the view that anything excreted by the fungus itself or by the host-plant acts as a solvent agent. Fungus spores, while actually germinating, or the mycelium while in a state of activity, would doubtless excrete substances capable of dissolving copper compounds, and the leaves of some trees (*e.g.* the lime), certainly do so, as do the leaves of many other trees when bruised; but no such action has yet been established, either with dormant fungus spores or with the sound leaves of fruit trees. The protective action of a fungicide consists in its forming a coating on the leaf, generally of copper carbonate, which is slightly soluble, and which, therefore, prevents fungus spores from germinating there. But protection may also occur through the imbibition of soluble copper into the substance of the leaf itself, for it has been shown that copper is thus absorbed, becoming apparently substituted for the iron which is normally present therein. It appears that both the fungicidal and the scorching action of soluble copper compounds is dependent solely on the amount of copper contained in them, unless the acid radicle present has a fungicidal action of its own, and the intensity of the effect is approximately a logarithmic function of the strength, so that often very little is gained by a considerable increase in strength.

The use of copper compounds originated in verdigris having been applied to roadside vines to prevent depredations, with the result that such vines were found to remain free from mildew. This led to the use of copper sulphate, to which lime was next added to neutralise the acid, which was supposed to be responsible for the scorching produced. Such a mixture was known as Bordeaux mixture, and it is still the most extensively used fungicide. The proportions of ingredients recommended have varied largely at different times, but at present it is generally made with 8 lbs. of lime and 8 lbs. of copper sulphate to 10 gallons, and it is obtained in the most satisfactory state of subdivision by adding the sulphate in the form of a strong solution to the lime, previously slaked and mixed with the bulk of the water. The action of lime on copper sulphate results in the formation of a series of basic salts, of which $4CuO,SO_3$ is the lowest, and is that formed when the lime is just sufficient to precipitate the whole of the copper. When the amount of lime is increased until the liquid becomes barely alkaline, the compound formed is $10CuO,SO_3xCaSO_4$, which is a very bulky substance, settling slowly in the liquid, and very suitable, therefore, for spraying. With a still larger proportion of lime, such as is used for Bordeaux mixture, it is the latter body which is formed at first, as the water present is insufficient to allow the whole of the lime to react at once, but this excess of lime gradually dissolves, and the precipitate is converted into another compound, $10CuO,SO_3,2CaO$, mixed with copper cuprite, this mixture forming a violet-blue compact precipitate, little suited for spraying. Bordeaux mixture should, therefore, be used as soon as possible after preparation. Most of the basic sulphates are insoluble, but are decomposed by carbon dioxide reproducing copper sulphate, though only in amounts representing a small proportion of that used in making them, as is evident from the equations:

$$10CuSO_4+9CaO=10CuO,SO_3+9CaSO_4$$
$$10CuO,SO_3+4{\cdot}5CO_2=CuSO_4+4{\cdot}5CuCO_3,CuO$$

although the proportion liberated in this state is found to be considerably in excess of that here indicated, the additional SO_3 required for the production of the excess being derived from the calcium sulphate, which is not present as such, but as an integral portion of the basic sulphate itself. The copper sulphate liberated acts directly as a fungicide in the manner above indicated, whilst the copper carbonate formed supplies a protective coating to the leaf. With ordinary Bordeaux mixture there is considerable excess of lime present, which decomposes any sulphate as soon as it is formed, the practical result being that only 2 or 3 p.c. of the copper sulphate taken to make it becomes converted again into sulphate, whereas about five to twenty times that proportion is obtained (according to the vapour pressure of carbon dioxide present) when pure $10CuO,SO_3$ is used, but the reduction in the proportion of active fungicide in the case of the ordinary mixture is partially counterbalanced by an increase in the protective carbonate formed. With ordinary Bordeaux mixture it is only when the deposit dries up, and liquid communication between the particles of

lime and basic sulphate is interrupted, that any copper sulphate is formed by the action of carbon dioxide. It seems, too, that the sulphate cannot remain very long as such on the leaves, for it is gradually converted into carbonate by the calcium carbonate present.

It has been shown that carbon dioxide at the low pressure at which it normally exists in the air, does not react with the basic sulphates so as to liberate permanently the amount of copper sulphate indicated in the above equations; but carbon dioxide is evolved in large quantities from foliage, and the reaction actually occurring probably approximates to that indicated. Judging by the fungicidal results, the proportion of soluble copper liberated from the compound $10CuO,SO_3$ is about six times that liberated from ordinary Bordeaux mixture containing the same weight of copper, instead of twenty times as much, as experiments with pure carbon dioxide suggested. This superior efficiency of $10CuO,SO_3$ has led to its introduction on to the market in the form of a paste. The absence of solid particles of lime, which clog the spraying nozzles, and the avoidance of the labour of home manufacture, are advantages claimed for it; but important advantage probably consists in the reduction of the amount of copper distributed over the land by the spraying. Seedling plants are remarkably sensitive to the toxic action of copper, the effect of one part of the metal in 10,000,000 of water being recognisable on barley seedlings. Copper carbonate is soluble in rain-water to a much greater extent than this, and the amount of copper reaching the soil in a single spraying would be sufficient to convert the soil-water in the upper nine inches into a solution containing enough of the metal to render it markedly toxic. So far as casual observations go, no deterioration of soil has been observed as a consequence of Bordeaux spraying, indicating that the ultimate compound formed by the metal must be a body less soluble than the carbonate, but until more is known on the subject, it is eminently desirable to diminish the accumulation of copper in the soil as much as possible. Herbage under trees may also become poisoned by copper spraying. Former experiments on this point had indicated that no such danger existed, but an instance has occurred in which a large number of sheep were killed by copper poisoning in a grass orchard which had been sprayed. Fruit should not be sprayed with copper within 5 or 6 weeks of its ripening.

Various dried Bordeaux mixtures are in use as substitutes for the ordinary mixture. They consist mainly of the basic sulphate $4CuO,SO_3$, and generally contain some soluble copper. The amount of soluble sulphate liberated from them by the action of carbon dioxide is much less than that indicated by their composition, the comparatively large particles of which they are composed becoming encased in the carbonate formed, thus preventing the completion of the action. They are comparatively dense powders, which renders them inferior as spraying materials.

Copper carbonate itself is sometimes applied direct to the trees, as a substitute for Bordeaux mixture, and is known as soda Bordeaux or Burgundy mixture. It is made by mixing 1·84 lbs. of crystallised sodium carbonate with 1 lb. of copper sulphate to make 10 or 20 gallons of wash. The precipitated carbonate consists of $5CuO,2CO_2$, some of this (to the extent of 0·003 p.c. of copper) remaining dissolved; but more copper is found in solution if either a smaller or larger proportion of sodium carbonate is used, a cupri-carbonate being formed in the latter case. The precipitated carbonate soon becomes granular and compact, changing into malachite, $2CuO,CO_2$, so that the wash should be used at once after being made. The large amount of copper contained in it is a disadvantage, and the acid sodium carbonate, present as one of the products of the reaction, is liable to injure delicate foliage (*cf.* Mond and Heberlein, Chem. Soc. Trans. 1919, 115, 908).

The addition of treacle to Bordeaux mixture has been advocated as a means of rendering some of the copper soluble, and also of increasing its adhesive properties. If the mixture is made with pure materials, the copper present dissolves in the dextrose of the treacle, either entirely or partially, according to the proportions, to give a violet solution which begins decomposing almost at once with the liberation of cuprous oxide. Such a mixture may either be very rich in dissolved copper or may consist of nothing but cuprous oxide, and is clearly very unsuitable for a spray fluid.

Numerous other copper compounds have been tried as substitutes for Bordeaux mixture, but without much success. Several of them are cuprammonium compounds which present difficulties in preparation of definite strengths, and there is much risk with them of the ammonia injuring foliage. Copper sulphate itself may be used, up to a strength of 0·25 p.c. copper, on trees while dormant.

C. **Detergent washes.** Lime-washing the trunks and main branches of trees has long been practised as a means of cleansing them and reducing insect attacks. The substitution of caustic soda for the lime produces more satisfactory results, and permits of the whole tree being treated by spraying. A wash containing $2\frac{1}{4}$ p.c. of caustic soda is recommended, and its efficacy is further increased, both as a detergent, and still more as a direct insecticide, by the addition of about 6 p.c. of paraffin oil, this being emulsified with it by the agency of the basic sulphates of iron or copper. A recipe, the origin of which is unknown, is very widely circulated, in which about half of the above quantity of caustic soda is supplanted by an equal weight of potassium carbonate; but it has been proved that the latter is practically valueless as a detergent, and the use of it merely entails loss of money and efficiency.

Gases.

Hydrocyanic acid is used in the fumigation of hot-houses for the destruction of plant lice, &c.; it is also used in many countries for disinfecting imported nursery stock, and in California it is applied to peach trees in plantations for scale, each tree being covered with a tent during the operation. To avoid danger to the operator, potassium cyanide is wrapped up in paper, and lowered from outside by means of a string into a jar of dilute sulphuric acid.

This is not always satisfactory, as the paper sometimes becomes converted into parchment paper and the cyanide becomes coated with potassium sulphate, which arrests the action. A better method is to enclose the cyanide in a little zinc canister made for the purpose and place the whole in the acid. For each 100 cubic feet of space, $\frac{1}{3}$ to $\frac{1}{4}$ oz. of 'lump' potassium cyanide is used, and for each ounce of the cyanide, one liquid ounce of acid previously diluted with 3 to 4 ounces of water. 'Stick' cyanide contains only 40 p.c. of potassium cyanide, and proportionately larger quantities of it must be used, whereas if sodium cyanide is taken (which is preferable on account of its being more easily soluble), the above quantities must be reduced by 25 p.c. Hydrocyanic acid is liable to cause some injury to young plants, and in fumigating these they should not be exposed to the direct stream of gas as it ascends from the generating vessel. Its action in destroying insect eggs is somewhat uncertain, and in the case of green-houses it is often necessary to repeat the fumigation after a fortnight's interval, to destroy insects which have hatched out from the eggs. For freeing nursery stock from woolly aphis, an advantageous substitute for fumigation is to immerse the trees bodily in water at 115°F. for 10 minutes.

Sulphur, as already mentioned, probably acts as an insecticide owing to its volatility, and it is often used for fumigating houses by heating it, taking care not to let it catch fire. Smouldering tobacco and pyrethrum are used in the same way. See also Fungicidal Properties of certain Spray Fluids, Horton & Salmon (Journ. Agric. Science, 1922, 12, 269). P. S. U. P.

PLASMA *v.* Quartz.

PLASMON. Milk casein made soluble by alkalis.

PLASTER OF PARIS *v.* Calcium.

PLASTERYL. An explosive consisting of a mixture of trinitrotoluene (99·5 parts) and resin (0·5 part).

PLASTIC CLAY *v.* Clay.

PLATINITE, PLATINOID *v.* Nickel.

PLATINO. Trade name for an alloy of 11 p.c. platinum and 89 p.c. gold, used as a substitute for platinum. It is more resistant to caustic potash than platinum, and does not become brittle when heated in a smoky flame. It is, however, attacked by sulphuric acid containing nitric acid (van der Marck, Pharm. Weekblad, 1918, 55, 149).

PLATINOTYPE PROCESS *v.* Photography.

PLATINUM. Sym. Pt. At.wt. 195·2. In the group of the platinum metals are included platinum, iridium, rhodium, palladium, ruthenium and osmium. They are almost entirely obtained from the crude 'platinum' which, originally present in traces in the older plutonic rocks, has become concentrated in the alluvial deposits derived from their disintegration.

The crude platinum is found in these alluvials as water-worn, rounded or flattened grains or nuggets or, very rarely, as cubes or octahedra, together with brighter, almost micaceous flakes of the alloy of iridium and osmium known as osmiridium or iridosmine. True nuggets are extremely rare, although one from the Urals, weighing over 250 oz., is exhibited at the Demidoff museum in Petrograd, and one weighing about 24 oz. has been found in Colombia. Platin-iridium, an alloy of platinum and iridium practically free from osmium, is also commonly associated with the ordinary crude platinum, while native palladium occurs with native platinum and in association or alloy with gold in Brazil, the Republic of Colombia, the Harz, New South Wales and Tasmania, and in copper-nickel ores in Ontario, Wyoming, &c.

Chromite, magnetite, ilmenite, and other heavy minerals which occur in serpentines and other alteration products of the parent rocks, are also found together with gold, in association with the crude platinum, but it is curious that, although gold and tin commonly occur together in alluvial deposits and, like the rare minerals tantalite, columbite, molybdenite, monazite, &c., are derived from plutonic rocks similar to those yielding platinum, they do not commonly occur in alluvials which are sufficiently rich to be worked for that metal.

Platinum occurs in minute traces in most river-beds the sands of which come from the older rocks, and has been found in dolomite, barytes, wollastonite, and many other rock-forming minerals produced by the metamorphism of such rocks, and in the metalliferous minerals associated with them. The presence of copper and iron in alloy with platinum in most varieties of crude platinum from the most widely separated districts is interesting, and the fact that it has been found in meteoric iron with nickel and in the cupriferous nickel ores of Sudbury in Ontario is deserving of special mention. The actual commercially workable sources of platinum are extremely limited, and there is no reason to anticipate the discovery of any new fields which are likely to add materially to the production except as/by-products from smelting operations.

Crude platinum commonly contains sufficient iron to be magnetic.

As platinum in the compact form does not amalgamate with mercury, the removal of native gold from native platinum is a simple matter, but this very fact results in the loss of much of the latter metal in alluvial workings where platinum occurs in small proportion as compared with the gold and is, in too many cases, allowed to pass away with the waste from the amalgamation. It is impossible to estimate the extent of this loss, but it is a fact that increasing proportions of platinum and the allied metals are being recovered in the refining of bullion obtained from alluvial gold, and that all ordinary refined gold contains platinum and iridium. From this source and from the treatment of the matte from the smelting of the nickel-bearing ores of Sudbury—where the mineral sperrylite (platinum arsenide, $PtAs_2$) occurs with nickeliferous pyrrhotine—of the copper ores of Wyoming, and of the ores of lead and silver which commonly contain platinum in traces, a considerable increase in the production of the platinum metals may be hoped for; but there is no reason to expect any material increase over the present alluvial output, and no ore *in situ* rich enough in platinum to justify direct treatment for its recovery, has yet been discovered. The fact that platinum cannot be amalgamated with mercury or profitably extracted by alkaline cyanide, renders it impossible to treat platiniferous ores similarly

to gold ores, even if they occurred to the same extent and were of the same richness as the latter. In this connection, it may be stated that the United States Geological Survey Report on the Production of Platinum, &c., for 1921, estimated the production of platinum in the United States in 1920, as about 488 oz.

Selected platiniferous nickel ore from Sudbury and the copper-nickel matte obtained from the smelting of the ore, have been treated by the Port Orford Copper Company in the United States and by others, for the extraction of platinum and the allied metals, and there is good reason to hope that a substantial increase in their production will be obtained from this and similar sources.

It is impossible to obtain trustworthy statistics as to the total world's production of either crude or refined platinum. The official figure for Russian production of crude platinum in 1916 is 63,900 oz., and in 1917 is estimated at 50,000 oz., which represents a considerable falling off from 300,000 oz. in 1912 and 250,000 oz. in 1913. In other countries, the statistics commonly include much old platinum which has been worked up, while, in some cases, part of the official figures are for real platinum and others for crude, *i.e.* for raw alluvial concentrate yielding anything between 60 p.c. and 80 p.c. of platinum with perhaps 10 p.c. of other metals of the platinum group.

The following figures issued by the United States Geological Survey in Sept., 1921, include probably the most accurate estimates of the production of the principal producers in 1919 and 1920. The production is given in troy ounces of crude platinum (which may be taken as roughly containing 70 p.c. of platinum).

	1919	1920
Russia	30,000	35,000
Colombia	35,000	35,000
United States	824	613
New South Wales and Tasmania	1,883	2,000
Canada (Tulameen, B.C.)	30	25

The following analyses are sufficiently typical to indicate the general character of crude platinum, &c., from various localities. They are somewhat old (the first five being by Deville and Debray) and the ruthenium has been ignored except in the case of the osmiridium, but they are probably as trustworthy as any which have been published :—

——	Pt	Ir	Os	Rh	Pd	Ru	Au	Cu	Fe	Osmiridium	Sand
Crude Platinum											
Choco (Colombia)	86·2	0·85	—	1·40	0·50	—	1·00	0·60	7·80	0·95	0·95
California	85·5	1·05	—	1·00	0·60	—	0·80	1·40	6·75	1·10	2·95
	79·85	4·20	—	0·65	1·95	—	0·55	0·75	4·45	4·95	2·69
Australia	61·40	1·10	—	1·85	1·80	—	1·20	1·10	4·55	26·00	1·20
Urals	76·40	4·30	—	0·30	1·40	—	0·40	4·10	11·70	0·50	1·40
,, (Nischnei-Taglisk	75·10	2·60	2·30	3·50	1·10	—	0·40	1·00	8·10	0·60	—
Borneo	70·21	6·13	1·15	0·50	1·41	—	—	0·34	5·80	—	—
Platin-iridium											
Urals	19·64	76·85	—	—	0·89	—	—	1·78	—	—	—
Brazil	55·44	27·79	—	6·86	—	—	—	3·30	4·14	—	—
Osmiridium											
Urals	10·08	55·24	27·23	1·51	trace	5·85	—	trace	trace	—	—
California	—	53·50	43·40	2·60	—	0·50	—	—	—	—	—
Australia	—	58·13	33·46	3·04	—	5·22	—	0·15	—	—	—

See also Koifmann (Arch. Sci. Phys. Nat. 1915, [iv.] 40, 22).

The purest nugget yet analysed contained 86·5 p.c. of platinum. They usually contain between 70 p.c. and 85 p.c., iron being the principal impurity, although copper is invariably present. In one nugget from the Urals, 19·5 p.c. of iron has been found.

Crude platinum is separated from alluvials by ordinary hand sluicing or dredging operations, and may be regarded as a by-product in gold dredging in the United States, Canada, Colombia, and many other districts, and as the main product in the Urals which, from five districts, is stated to have produced before the war about 95 p.c. of the world's output. In the Urals, about 80 p.c. of the total yield is at present obtained by hand sluicing, but dredging is superseding hand work in re-treating many of the old dumps.

The metal occurs in an eroded peridotite covering a large area, but, although increased activity has arisen through the rise in the price, production is almost stationary, and any increase must be dependent upon dredging operations dealing with deposits too poor to permit of treatment except on an enormous scale and under more economical conditions. A large proportion of the total production is smuggled across the frontier, and it is believed that the officially certified output of 176,716 oz. of crude platinum for 1910, should be increased by at least 100,000 oz., to allow for such illicit and other additional production.

Since 1914 the official figures for the Russian output of platinum mineral has decreased from 155,838 oz. in that year to 106,778 oz. in 1916, and probably less than 100,000 oz. for 1917.

It has been stated that the alluvial treated in Russia averages between 30 and 35 grms. of crude platinum per ton, but this probably refers to the material actually washed by hand labour and ignores the overburden which has first to be removed. It is probable that the material actually handled averages under one-third of that amount, or well under one part per million.

Apart from Russia, the most important producer is the republic of Colombia which in 1910 yielded, from two districts on the Pacific side of the state, about 10,000, and before the war about 15,000 oz. a year. The estimated amount for 1917 was 32,000 oz. crude platinum. The output of platinum in Colombia is, however, so small in comparison with the gold, which constitutes the main value of the alluvials, that the industry has not hitherto been regarded of especial importance, although the total production to date is stated to have exceeded half a million ounces of crude platinum, and although platinum was obtained from Colombia or, at any rate, from South America, nearly a century before it was discovered in Russia. Modern dredging methods, however, are now coming into use in the Choco and Condoto districts, an area of about 90 by 30 miles.

In 1819, grains of a white metal were found in the auriferous gravels of the Urals, and in 1823, the metal was proved to be platinum. From 1825 to 1845, the Russian Government absorbed all the output for their coinage, but in that year such coinage was discontinued, and a heavy fall occurred in the price previously commanded by Colombian platinum and, until recently, platinum has only been produced in South America by natives operating with the crudest appliances and only when necessity compelled them to work.

The chief markets before the war where the bulk of the platinum mineral was refined were in England, France, and Germany. The other metals of the platinum group are present only in small proportion, and their recovery, notwithstanding their importance and high market value, is entirely dependent on the amount of crude platinum obtained by the miner or concentrated by the smelter, and the skill with which it is worked up by the metallurgist.

It is interesting to note that Messrs. Johnson, Matthey and Co., who introduced autogenous soldering with the oxy-hydrogen blowpipe and who are still the largest refiners of the metal, were the first to engage in the industry as a commercial enterprise and have throughout been the most active in introducing improvements in the metallurgical and chemical treatment of crude platinum, in producing the various platinum metals in a state of purity or as alloys of definite composition and for special uses, and in generally developing both the commercial and scientific sides of the industry. From the point of view of the analyst and physicist, probably no rare metals are of such importance in their work or so difficult to obtain in a condition suitable to their requirements.

At the close of the eighteenth century, Marggraf, Achard, and others prepared a platinum crucible by igniting an alloy of platinum and arsenic, and hammering up the mass of malleable platinum thus left and, for some years from 1787, Jeanety, a working silversmith, employed the method commercially in Paris. The metal was, however, very impure. It failed to withstand high temperatures and was unsatisfactory for the fusion of alkaline carbonates. The precipitation of the double chloride of platinum and ammonium, and the presence in it of the red iridium salt, were known even at that period, and Count Puschkin, Vice-President of the Department of Mines of St. Petersburg, referred to it in 1797 as well known and, at the same time or a year or two later, suggested the use of the precipitate as a means of preparing pure platinum after first converting it into an amalgam with mercury.

Between the years 1800 and 1808, Thomas Cock, a relative of Mr. Percival Norton Johnson, the founder of the firm of Johnson, Matthey and Co., elaborated the method of dissolving the crude metal in *aqua regia*, precipitating it as the double chloride of platinum and ammonium, and igniting the washed precipitate to spongy platinum under conditions which render it suitable for being hammered and worked up into crucibles, &c. This process, which was afterwards commonly known as Wollaston's, on account of his having described it, with many improvements, in the Bakerian lecture for 1828, is fully described in many works on Chemistry. and is the basis of all present methods of refining platinum. The insoluble matters left by the *aqua regia* treatment contain osmiridium and various impurities, such as chromite, zircon, spinel, &c., originally present in the crude platinum, while the mother-liquor from the double platin-ammonium precipitate contains most of the rhodium, palladium, and ruthenium, together with a small proportion of the iridium and osmium. The insoluble matter and the mother-liquor are both worked up for the separation of these metals.

The solution obtained by acting on the mineral with *aqua regia* is boiled down with enough hydrochloric acid to free it completely from nitric acid, and this attack is repeated until the mineral residue, or a sample taken out, loses no more weight with further treatment. The clear liquor is freed from gold by adding a ferrous salt or a sulphite. After settling and drawing off the clear solution, the platinum and part of the iridium, as already stated, are precipitated with a solution of ammonium chloride. The mother liquor contains so much iron, copper, and other impurities that it is usually treated at once with clean scrap iron or zinc, and the whole of the values, together with the copper and other reducible metals, thrown out as a black flocculent precipitate, which is, however, easily filtered and washed. The treatment of this precipitated residue, containing all the palladium, most of the rhodium, and some iridium and platinum, and of the insoluble residue containing the osmium, most of the iridium and small quantities of the other metals, have been the subject of much investigation for over a century, since Wollaston discovered rhodium and palladium in 1805. A single complete method for separating all the six 'platinum metals' in any proportion is not a practical problem, and reactions and procedures adapted for an assay method or for working on an ounce or two are often quite unsuitable for the large scale.

The principal facts to be kept in mind are (1) that the chlorides are by far the most stable of the compounds and the most easy to prepare; (2) that platinum is not easily reduced from $PtCl_4$ to $PtCl_2$ in acid solution, while iridium is very readily reduced from $IrCl_4$ to $IrCl_3$, and easily oxidised back again; (3) that rhodium is present in acid solution as $RhCl_3$

only; and (4) that palladium exists as $PdCl_2$ and is unstable as $PdCl_4$. The sodium chloride double salts are all extremely soluble, while the potassium or ammonium salts of the type MCl_4, or rather K_2MCl_6, are very nearly insoluble, but of the type MCl_2 and MCl_3 are fairly soluble though not so soluble as the sodium salts. The volatility of OsO_4 from an acid solution in a stream of chlorine is usually taken advantage of, while the ready solubility of palladium in nitric acid differentiates it from the other five metals. Palladium is also easily reduced to metal from chloride solution, *e.g.* by passing hydrogen or acetylene or by adding hot ferrous sulphate to the boiling solution. In the following summaries of separation methods only the essentials are recorded. The original memoirs must be consulted for full working details.

The insoluble residue after *aqua regia* treatment of the mineral may be purified to yield clean osmiridium by careful grinding, washing, and sieving, but the washings always contain very fine and flaky metal. Carl Claus, the father of the chemistry of the platinum metals, in a fine monograph (Beiträge zur Chemie der Platinmetalle, Dorpat. 1854) attacks this insoluble residue by fusion with potash 1 part, and nitre 2 parts, in a silver or iron crucible. The melt is poured on to a cold iron plate, broken up and dissolved in cold water. The clear liquor is decanted and most of the ruthenium precipitated by neutralising with nitric acid. It must be boiled with *aqua regia* to free it from osmium. The portion of the melt insoluble in water is dissolved in *aqua regia* and also distilled for OsO_4, leaving iridium as $IrCl_4$, which, after filtration, is precipitated by potassium chloride and washed with a weak solution of the same salt until free from rhodium and ruthenium. Claus attacks the precipitated residue, after a preliminary purification with weak acid and then potash, by Wöhler's method, namely, heating the dried powder mixed with its own weight of salt to dull redness in chlorine. The filtered solution is oxidised by nitric acid to convert the iridium into $IrCl_4$, and the iridium and platinum precipitated by ammonium chloride. The rhodium is washed out of this mixed precipitate by weak ammonium chloride solution and the liquors evaporated to crystallise the ammonium rhodium chloride. The crude iridium salt, containing platinum, is boiled up with water and the $IrCl_4$ reduced to the soluble olive-green $IrCl_3$ by sulphuretted hydrogen and freed from small quantities of rhodium and ruthenium by recrystallising. The platinum salt left behind is boiled with *aqua regia* to oxidise any sulphide formed and reprecipitated with sal-ammoniac.

Wolcott Gibbs (Amer. J. Sci. 1861, [2] 63; 1862, 341; 1864, 57) attacks the osmiridium residue in the same way and collects the distilled OsO_4 in alcoholic potash, forming the crystalline potassium osmate. In treating the crude iridium salt precipitated from the residue left in the distilling flask advantage is taken of the fact that sodium nitrite in hot water dissolves the iridium, ruthenium, and rhodium, leaving most of the platinum unchanged as K_2PtCl_6, while sodium sulphide added to the nitrite solution precipitates only the ruthenium, rhodium, and platinum, leaving the iridium in solution. The sulphides of the three metals are converted back into their double chlorides with potassium and treated this time with potassium nitrite, since only the ruthenium potassium nitrite is soluble in absolute alcohol, with which the dried mass is extracted. By repeated boiling and evaporation with water the rhodium potassium nitrite, which exists in two forms, soluble and insoluble, is all converted into the insoluble form, from which the platinum salt can be washed by boiling water. The nitrites are all readily converted into chlorides by boiling with hydrochloric acid.

A modification of this process is due to Liedié (Compt. rend. 1900, 131, 888; and Chem. News, 1901, 83, 19). The mixed chlorides obtained by heating the metals with salt in dry chlorine are converted into nitrites by boiling with sodium nitrite, enough sodium carbonate being added to render the solution neutral or just alkaline. All base impurities are thus precipitated and may be filtered off. The solution is made strongly alkaline with caustic soda and the osmium and ruthenium distilled off with chlorine as described later. The residual metals are once more converted into nitrites with sodium nitrite and, after cooling, enough ammonium chloride is added to cause the double ammonium nitrites of rhodium and iridium to crystallise, since they are both almost insoluble in a cold solution of sodium nitrite and ammonium chloride, with which they may be washed. The platinum and palladium are recovered from the mother-liquor.

Bunsen (Annalen, 1868, 146, 265) first separates palladium from the impure mixed metals by means of its superior solubility in weak *aqua regia*, and precipitates potassium palladic chloride from this solution by prolonged shaking with chlorine in a closed flask. The metallic residue is cleaned by a fusion with ten times its weight of zinc melted under zinc chloride and cleared with sal-ammoniac. The button is parted in hydrochloric acid and the metallic powder after washing and careful drying, for it is liable to explode if overheated, is mixed with dehydrated barium chloride and attacked by heating in a stream of dry chlorine. The barium is precipitated from the resulting solution by sulphuric acid and the base-free solution of iridium, rhodium, platinum, and some palladium reduced at 100° with hydrogen. Palladium and platinum are precipitated first. In the liquor the rhodium and iridium are converted into their double sodium sulphites, which are insoluble in hot alkaline sulphite. The filtered sulphites are treated with strong sulphuric acid and the excess of acid evaporated at 400°, which leaves the rhodium as an insoluble pink double sodium sulphate while the green iridium sulphate is quite soluble.

Starting with metal, however, the most satisfactory procedure is due to Deville and Debray (Ann. Chim. Phys. 1859, [3] 56, 439) and Deville and Stas (Procès verbaux des Séances, 1877). When the mixed metals are melted at a high temperature with ten times their weight of lead they behave differently on cooling and parting in dilute nitric acid. The iridium, with ruthenium and osmium, remains as a fine grey crystalline powder unattacked by

any acids. The palladium goes into solution with the lead nitrate together with a little rhodium and platinum, especially if base metals or silver are present, while almost all the rhodium and platinum, retaining a little lead, are insoluble in the nitric acid used but soluble in *aqua regia*. Full details for the separation of the metals in the three portions are given in the papers referred to, but they follow the usual lines. The insoluble iridium, with ruthenium and osmium, is best attacked by fused potash and nitre. The liquor and the insolubles after dissolving in cold water are distilled in chlorine, separately if much ruthenium and osmium are present, or together if not. The distillate is passed first through one or more distilling flasks containing hydrochloric acid to collect the ruthenium and then into cold potash, with alcohol if it is desired to form the crystalline non-volatile potassium osmate. Chlorine is bubbled through the solution of the alkaline melt in a distilling flask in the cold to saturation and the temperature is then gradually raised to 70°, when the volatile metals pass over freely, and finally boiled with chlorine passing all the time. The acid flasks where the ruthnium is retained are similarly brought to the boil, and in this way all the osmium passes over into the alkali. A second fusion of the iridium residue with potash and nitre and subsequent distillation in chlorine may be necessary if much ruthenium or osmium are present or if the first attack has been incomplete.

Caustic soda 1 part, and sodium peroxide 4 parts, may be used to attack osmiridium or the insoluble from the lead melting if the presence of potassium salts is undesirable. The operation is conducted in a nickel crucible with constant stirring, as it forms a pasty and not a fluid melt. The solution of the cold mass in water must also be done carefully, owing to the rapid evolution of oxygen. This and various other improvements are due to Liedié and Quennessen (Bull. Soc. chim. 1902, [3] 27, 179; also Compt. rend. 1903, 136, 1399; and Chem. News. 1903, 88, 3).

It is impossible after a fusion with potash and nitre to wash away all traces of potassium from the mixed oxides. But a solution free from bases may be obtained by conducting the fusion with barium peroxide and nitrate and precipitating the barium from the subsequent hydrochloric acid solution with sulphuric acid.

Mylius and Förster (Ber. 1892, 25, 665) describe a method for detecting small amounts of impurities in metallic platinum which depends on the volatility of the compound of platinous chloride with carbon monoxide. Five to ten grams of the metal as thin foil are heated to about 240° by a bath of boiling quinoline in a tube through which is passed chlorine mixed with a little carbon monoxide. The whole of the platinum volatilises in six to eight hours. The metal can be recovered from the condensed distillate, which may also contain iridium, palladium, ruthenium, osmium, gold, and iron, while rhodium, silver, copper, and lead remain behind.

A complete analytical method for platinum mineral is given by Koukline (Rev. de met. 1912, 9, 815). This embodies in a convenient procedure many of the reactions already given.

Mylius and Mazzucchelli (Zeitsch. anorg. Chem. 1914, 89, 1) give a detailed account of a qualitative and quantitative analysis of 'nominally pure' and 'commercial' platinum. The purity of the metal may be quickly verified by treating a faintly alkaline 1 p.c. solution of the nominally pure metal with a few drops of sodium hypochlorite or hypobromite and warming. Impurities are shown by the solution darkening and giving a dark blue precipitate on standing. The content of iridium in platinum may be rapidly estimated by dissolving 0·01 gram of the metal in *aqua regia*, evaporating, making up the acid solution of the residue with water to 100 c.c., and comparing the colour with similarly prepared standard solutions of platinum containing a known quantity of iridium.

According to Wichers (J. Amer. Chem. Soc. 1921, 43, 1268; Chem. Soc. Abst. 1921, ii. 648) commercial platinum may be freed from the impurities it usually contains by repeated precipitation as ammonium platinichloride. A sample of platinum containing palladium, rhodium, and iridium, as well as tin, iron, and other metals, can be obtained pure by four such precipitations. Each precipitate of ammonium platinichloride is drained on a Buchner funnel, stirred with a considerable volume of 15–20 p.c. ammonium chloride solution, and again drained, this process being repeated two or three times. The washed precipitate is dried, ignited to platinum sponge in an electrically heated muffle, and dissolved in *aqua regia*. The solution is evaporated several times with hydrochloric acid to remove nitric acid and precipated with ammonium chloride. The amount of platinum left in the mother-liquor is usually not more than 1 p.c. of that in the precipitate. The final precipitate is ignited to sponge in a porcelain dish over a gas flame in a current of hydrogen (Chem. Soc. Reports, 1921, 57).

The important and increasing production of the platinum metals through concentration during the 'bessemerisation' and final electrolytic treatment of copper ores and, particularly, of the matte obtained from the nickel-copper ores of Sudbury, Ontario, and from the arsenical cobalt-nickel ores, associated with native silver in the cobalt district of Ontario, has already been mentioned. These and other metallurgical operations, in which the precious metals become naturally concentrated in a product requiring final electrolytic purification or acid treatment, are the only ones from which any substantial increase in the output can be expected, but they are sufficiently promising to deserve special attention from both metallurgist and chemist. No trustworthy information is available as to the exact procedure, but it appears to be mainly confined to the treatment of the anode mud obtained during the final electrolytic purification of the metals or the residue left by the acid or other treatment of the matte. The 'mud' or residue contains the gold, silver, and platinum metals together with selenium, bismuth, &c., and is melted down and refined by ordinary chemical processes. Such details and general information as are available will be found in the Royal Ontario Nickel Commission Report (Toronto, 1917).

In 1915, over 1500 oz. of palladium, in

addition to 6500 oz. of platinum and an unknown amount of iridium, rhodium, and ruthenium, were produced in the United States from the treatment of bullion and blister copper.

Platinum is a white metal, capable of taking a high polish and, when pure, ranking next to gold and silver in malleability and ductility. Its sp.gr is 21·46 (G. Matthey), and its hardness, if pure and when annealed, is 38 (Brinell scale). It melts at 1710°+50° as determined with a resistance pyrometer by Harker, or at about 1753° as determined with the optical pyrometer by Waidner and Burgess; 1755° according to Dana and Foote. It is stated by Knocke to commence to volatilise *in vacuô* at 540°, while, according to Hulett and Berger, volatilisation commences at 800° in air, but does not occur in the absence of oxgyen. The extent of such volatilisation is, however, still doubtful and, under normal conditions, is a matter of only slight technical importance, except in so far as it emphasises the necessity for cleanliness of utensils and special care in the method of heating and in ensuring perfect combustion of the fuel. The loss experienced with pure platinum vessels at the strongest heat to which they are ordinarily subjected is known to be negligible, although Moissan has volatilised it and the other platinum metals, in the electric furnace.

The specific heat of platinum between 20°–300° is 0·03271, and the true specific heat at 300° and above is given by the expression $0{\cdot}031686 + 0{\cdot}0000364\theta$ (White, Phys. Rev. 12, 346, 1918).

An interesting method of determining the purity of platinum ware is due to Burgess and Sale (J. Wash. Acad. Sci. 1914, 4, 282). Two pieces of pure platinum wire are fused to the opposite sides of the dish or crucible and the junctions kept at different temperatures, ascertained by independent thermocouples. The two wires are connected to a suitable millivoltmeter and from the E.M.F. generated between the hot and cold junctions the purity of the platinum vessel can be ascertained by comparison with known standards. In a later paper (*ibid.* 1915, 5, 378) the authors give the losses on heating crucibles made of pure platinum and of alloys with rhodium and iridium (*also* Burgess and Waltenberg, J. Ind. Eng. Chem. 1916, 8, 487).

The expansion of platinum when heated is less than that of any other single metal, its coefficient of linear expansion being 0·00000907 at 50° according to Fizeau, or 0·00001130 at 1000° according to Le Chatelier. This expansion being about equal to that of ordinary glass, has resulted in the use of platinum for a large variety of electrical purposes, and there is a constant increase in the gross consumption for the leading-in wires of electric lamps, although improvements in the construction of the lamps themselves have resulted in less platinum being employed per lamp. For the same reason, *i.e.* because its expansion is about equal to that of the material of which the best artificial teeth are made, very large quantities of platinum have been used in dentistry, in addition to its employment in alloy with silver. Its high melting-point and great electrical resistance, and the absence of oxidation, render it the best medium for localising the heat and economising the current in electric furnaces for scientific purposes where efficiency and convenience are more important than saving in cost.

Platinum specially refined and absolutely free from iridium is used in the form of fine wire in resistance thermometers. The presence of iridium not only alters the curve of resistance increase with rise of temperature, but also, owing to its superior volatility, causes the wire to change slightly at a prolonged high temperature. For the same reason a thermojunction of pure platinum with 10 p.c. rhodium is preferred to one with 10 p.c. iridium, for although the latter gives a higher E.M.F., the junction gives a falling value with use and disintegrates much sooner than the 10 p.c. rhodium junction (*see* Sosman, Amer. J. Sci. 1910, 30, 1; Day and Sosman, *ibid.* 29, 93).

Although the most useful of all metals for general scientific purposes, it is attacked by many reagents which would scarcely be expected to have any action upon it, and the greatest care is essential in its use. Practically all other metals will alloy with it, and all—excepting certain of the other platinum metals—lower its melting-point. For this reason, no metal or metallic compound in presence of a reducing agent should be heated in it, nor should cyanides, sulphides, or arsenides, or arsenates or phosphates (in presence of a reducing agent or, practically speaking, under any circumstance) be heated in it. Caustic alkalis or alkali nitrates or the alkaline earths or peroxides or per-salts generally should also not be fused in it, as they attack and partly dissolve the metal as well as tend to render it permanently brittle, on the other hand, fused bisulphate does not attack compact platinum and is a useful reagent for cleaning dirty metal. Fused ammonium sulphate or the halogen salts of the alkali metals have little or no action upon it, but a mixture of this sulphate with ammonium or potassium bromide, corrodes it rapidly.

The power of platinum (referred to later) to occlude gases, has doubtless much to do with the brittleness which the metal acquires if used without due care and without frequent burnishing to overcome the porosity which, at first only superficial, gradually extends to the interior, if not overcome by frequently rubbing down the surface. Acid salts and pure unmixed acids are practically without action upon it, and the demand for platinum for sulphuric acid concentration has accounted in the past for the locking-up of more of the metal than any other use. The first large piece of platinum apparatus for this purpose was made by Messrs. Johnson, Matthey and Co. It was capable of holding 300 lbs. of sulphuric acid and was employed over a hundred years ago by Sandman in the Borough, and at the Paris Exhibition of 1855, the makers first exhibited a gold-lined platinum still.

Of late years platinum has been largely replaced in sulphuric acid concentration by gold, and, more recently, by silica-glass or, where the presence of traces of iron is unimportant, by vessels of specially resistant alloys of iron and silicon. Its use in dental alloys, although always large, becomes substantially reduced when the price rises, so that much of the metal which would otherwise become permanently locked-up, is released for other

uses; while the employment of platinum and its alloys for self-lighting lamps—an extremely old use which became again fashionable during the last decade—has apparently been finally given up in favour of spirit lamps ignited by the spark from a pyrophoric alloy containing cerium and acting like flint and steel.

On the other hand, the use of platinum black as a catalysing agent (as referred to later) in the manufacture of sulphuric acid, is increasing rapidly and is causing the locking-up of a further large quantity of the metal; while its use in electro-chemistry and pyrometry and in the ignition system of explosion engines, and the collectively large and constantly increasing use of small pieces of platinum apparatus, add largely to the demand.

Perhaps the most serious and almost permanent loss of platinum is in the enormous consumption in dentistry, which is stated to account for over 60,000 oz. annually. An increasing amount was used in jewellery until it was prohibited in January, 1916, and at least two-thirds of the large quantity employed in the lamp and other electrical industries is permanently lost. The platinotype process of photography and the use of platinum salts in the production of permanent colours for pottery, &c., also account for a considerable permanent loss of the metal.

According to the U.S. Geol. Survey Report for 1921 over 57 p.c. of the platinum metals was consumed by jewellers, 19 p.c. by the electrical industry, 10 p.c. by the chemical industry, and 11 p.c. by dentists.

The power of absorbing gases, possessed by platinum has found a number of both purely scientific and commercial applications. Although massive platinum has the power of absorbing gases and is even porous to them, the value of the metal in this connection is mainly seen when it is in the form of spongy platinum or platinum black. Solid platinum will absorb 3·8 volumes of hydrogen gas at a red heat, and the gas will pass through platinum tubes at bright redness. The fact that many other gases and vapours are similarly adsorbed or occluded by this metal, has been taken advantage of in the glow-lamp of Davy and the lamp of Döbereiner. In each, the simultaneous occlusion of a combustible gas or vapour and oxygen from the air, brings the two into such intimate contact as to induce immediate combination. The heat of the combustion in the 'pores' of the metal, causes incandescence of the wire spiral in the case of the lamp of Davy or of the platinum sponge in the Döbereiner lamp.

Pure melted platinum will also dissolve oxygen like silver and palladium, but this is given out on solidifying (Deville, Compt. rend. 1870, 70, 256, 287; Ann. de chim. et phys. 1859 [3], 56, 419).

By careful adjustment of the conditions, either complete or partial oxidation may be attained, and many oxidation processes may be carried out automatically with suitably prepared platinum. One of the earliest to be tried on the commercial scale was the conversion of alcohol into acetic acid.

The preparation of platinum sponge and platinum black for catalytic purposes, requires care and experience. For the manufacture of the former, the double chloride of platinum and ammonium is ignited to drive off the ammonium chloride and the chlorine combined with the platinum at the lowest possible temperature, so that the sponge shall retain the maximum surface; or asbestos, pumice, or other porous material may be saturated with platinum chloride and ignited, so that a still larger surface is exposed. Platinum black, a far more active form of the metal, is obtained as a finely divided residue, by treating alloys of platinum and soluble metals with dilute acids; or, better, by precipitating the platinum from a weak solution of the chloride with a reducing agent. Platinum black is capable of absorbing over 800 times its volume of oxygen, a portion of which appears to enter into combination as platinum hydroxide. It forms an extremely powerful oxidising or catalysing agent and is frequently used as such in organic chemistry, but it rapidly loses a portion of its activity and becomes denser and of the nature of spongy platinum.

The only large scale catalytic process in which platinum is employed is the 'contact' process, in which sulphuric acid is manufactured direct from a mixture of sulphurous acid gas and air. This process, although long known, was not employed commercially until a demand arose for the strongest possible sulphuric acid for the manufacture of dyes, explosives, &c. The cost of evaporating the weak acid from the lead-chamber process or of preparing Nordhausen acid, and the increasing requirements of the trade led, however, to such improvements that 'contact' acid can be obtained of any necessary strength in terms of SO_3 dissolved in H_2SO_4 (*v.* SULPHURIC ACID).

The difficulties due to the rapid falling-off in the activity of the spongy platinum employed as the catalyser, have now been largely overcome, and the working up of the exhausted metal into fresh sponge has been simplified. The fact that arsenic rapidly 'sickens' the platinum, has rendered it necessary to remove that impurity from the sulphurous acid gas before oxidation, and the success which has attended such treatment has resulted in the production of acid remarkably free from arsenic and, at the same time, allowed the use of pyrites more arsenical than was previously permissible.

Such purification is largely effected by the use of iron oxide which, while removing arsenic with formation of ferric arsenate, oxidises much of the sulphurous acid. Many other catalysers have been employed with success, but none result in so complete a conversion of the sulphur dioxide into the trioxide and, even when they are employed, the aid of spongy platinum is generally required for the completion of the reaction.

Gauze or foil of metallic platinum, free from iridium and iron, is also used in Ostwald's process for oxidising a mixture of ammonia and air to form the peroxides of nitrogen (*see* Partington, J. Soc. Chem. Ind. 1918, 37, 337 R).

The electrolytic action induced by the presence of a minute trace of platinum has a remarkable effect in promoting the solution of many metals in acid or other solvents, and in increasing their activity as reducing agents, &c. As platinum is so readily reduced by metals, the addition of a few drops of platinum chloride

to the solution in which the metal lies, will often suffice for a large quantity of metal at a negligible cost, so that the application of this property which, although well known, has not yet been commercially employed, is well deserving of attention.

Platinum may be deposited quantitatively by electrolysis and free from iridium if a low voltage is used. Plating to give a bright adherent deposit is best accomplished from a bath containing 4 grams platinum chloride, 20 grams ammonium phosphate, 90 grams sodium phosphate, and 5 grams sodium chloride per litre. The article to be plated should be kept in motion and the bath should be warm.

Although platinum can be readily alloyed with most metals, the alloys of industrial importance or even of scientific interest are few. As a rule, the qualities which render platinum valuable in the arts are destroyed by the presence of other metals, even in small quantities, and the addition of small quantities of platinum to other metals results in no improvement. The alloys of gold and platinum are of little importance, although of considerable interest on account of the fact that all bullion contains at least a trace of platinum, and that bullion is now largely treated electrolytically for its recovery. An alloy containing 70 p.c. of gold and 30 p.c. of platinum is only slightly yellow while, when more than 35 p.c. of platinum is present, no sign of yellow colour appears. Gold containing 5 p.c. platinum is harder and more resistant than fine gold, and may be used for vessels or appliances where gold alone is too soft.

The platinum-silver alloys are of interest on account of their use in dentistry and, to some extent, as a solder for platinum, but mainly because the solubility of platinum so alloyed in nitric acid, and the insolubility in sulphuric acid, are utilised in the separation of platinum from gold and in the assay of ores supposed to contain platinum. For the latter purpose, an ordinary fire assay is performed exactly as for a gold ore, so that the platinum becomes collected in a button of lead together with any gold and silver which may be present. After the lead has been removed by cupellation, the silver may be removed (leaving the gold and platinum) by heating with sulphuric acid diluted with about one-fifth of its volume of water, or both the silver and platinum may be entirely dissolved (leaving the gold), by heating with dilute nitric acid. To ensure complete solution of the platinum in nitric acid, not less than 10 parts of silver to 1 of platinum must be present.

Further details of the action of nitric acid on alloys of silver containing platinum are given by Koifmann (Arch. Sci. Phys. Nat. 1915, [iv.] 40, 509).

The alloys of platinum and iridium are of great value and of increasing importance. The presence of even a small quantity of iridium in platinum increases its hardness and generally adds to its resistance to heat and to corrosion by reagents. The alloy containing 10 p.c. of iridium has been employed in the manufacture of standard weights and measures and, as already stated, with pure platinum, for the thermo-couples of pyrometers. An alloy containing 10 p.c. of iridium was employed by Mr. George Matthey in preparing the standard measures of length for the International Standards Committee. He afterwards recommended a 15 p.c. alloy for that purpose, and a 20 p.c. alloy as the best for standard weights.

Alloys up to 30 p.c. iridium have a commercial application, chiefly for contacts for the ignition circuit of explosion engines, a use which has increased very greatly since 1914. The hardness of the alloy increases with the proportion of iridium; thus 5 p.c. is 85, 10 p.c. is 110, 20 p.c. is 200, 25 p.c. is 230, and 30 p.c. is 260 (Brinell numbers for annealed metal), but above this percentage of iridium the metal is so hard as to be brittle and difficult to work at ordinary temperatures without gaining any corresponding advantage. The alloy with 10 p.c. iridium is slowly but completely soluble in strong, hot *aqua regia*, but the richer alloys are scarcely attacked even by prolonged action.

The selling price of platinum in London in shillings per oz. troy since 1877 is given in the following table:—

1877	..	30	1905	..	$82\frac{1}{2}$–$85\frac{1}{2}$
1887	..	31	1906	..	$88\frac{1}{2}$–150
1889	..	45	1907	..	140–100
1890	..	70	1908	..	100– 90
1895	..	46	1909	..	90–120
1896	..	$48\frac{1}{2}$–52	1910	..	$123\frac{1}{2}$–154
1897	..	56	1911	..	160–185
1898	..	$57\frac{1}{2}$–60	1912	..	185
1899	..	65–71	1913	..	185
1900	..	72–$78\frac{1}{2}$	1914	..	185
1901	..	80	1915	..	190–290
1902	..	80	1916	..	200–290
1903	..	80	1917	..	290
1904	..	$75\frac{1}{2}$–$81\frac{1}{2}$	1918	..	400

The New York (U.S.A.) prices for platinum, palladium, and iridium are quoted weekly in the Engineering and Mining Journal.

Although all the compounds which platinum forms with the non-metals are decomposed by heat and commonly also by reducing agents, this metal probably forms a larger and more interesting series of salts than any other of the noble metals, its double salts with the alkalis and alkaline earths being especially interesting.

A bibliography of the metals of the platinum group: 1748–1917, by J. Lewis Horne and H. C. Holtz, forms Bulletin 694 of the U.S. Geological Survey, Washington. See also the Report on Platinum and Allied Metals (1922), published by the Imperial Mineral Resources Bureau.

Platinum Compounds.

Oxygen compounds. Platinum monoxide PtO, which gives rise to the platinous salts, is formed as a grey powder when the hydroxide is ignited carefully; or as a violet powder by igniting calcium platinate and treating the residue with nitric acid. When heated strongly it yields the metal, and when reduced with formic acid it gives platinum black. It forms a stronger oxidising agent than the dioxide, and a better reducing agent than platinum (Whöler, Zeitsch. anorg. Chem. 1904, 40, 423).

Platinous hydroxide $Pt(OH)_2$ may be formed by the action of caustic soda or potash on the dichloride, or, better, on aqueous potassium

platinochloride. It is an oxidising agent and acts as a weak base, some of the salts of which have been prepared.

Platinum dioxide PtO_2 is a black powder obtained by heating the corresponding hydroxide.

Platinic hydroxide or **platinic acid** $H_2Pt(OH)_6$, or $PtO_2 4H_2O$ or $Pt(OH)_4 2H_2O$ (Bellucci, Atti R. Accad. Lincei, 1903, [v.] 12, [ii.] 635; Gazz. chim. ital. 1905, 35, [ii.] 334; Blondel, Ann. Chim. 1905, [viii.] 6, 81), is prepared by boiling a solution of platinic chloride with caustic potash and treating the basic salt thus formed with acetic acid. When freshly prepared it is almost white, and is readily soluble in acids and alkalis, two of its hydrogen atoms being acidic and two basic. When dried, or on standing, it becomes yellow, and is no longer soluble in dilute acids. Platinic acid forms crystalline platinates of the type $M'_2Pt(OH)_6$, and also of a more complex constitution (Blondel, *l.c.*; Bellucci and Parravano, Atti R. Accad. Lincei, 1905, [v.] 14, [i.] 459; Gibbs, Ber. 1877, 10, 1384; Herschel, Phil. Mag. 1832, [ii.] 1, 58).

The oxides Pt_2O_4, Pt_2O_3 have been described (Jörgensen, J. pr. Chem. 1877, [ii.] 16, 344; Dudley, J. Amer. Chem. Soc. 1902, 28, 59), but it is doubtful whether they really exist (Wöhler, *l.c.*). The *hydrated platinum sesquioxide*

$$Pt_2O_3,xH_2O$$

intermediate between the two foregoing hydroxides, has been prepared by Wöhler and Martin (Ber. 1909, 42, 3958 and 4100).

Platinum trioxide PtO_3 is formed when the hydrated dioxide is electrolysed in a 2N solution of potash at 0°. A brilliant golden-yellow substance of composition $3PtO_3,H_2O$ separates at the anode, and the trioxide can be isolated by neutralising the alkali with very weak acids. It forms a red-brown substance which loses oxygen readily, but is scarcely attacked by dilute mineral acids. Most reducing agents reduce it to platinum black. It liberates iodine from potassium iodide, but has little effect on alcohol, acetic acid, or many oxidisable organic substances. Many of the hitherto observed reactions of platinum are said to be due to the formation of this oxide (Wöhler and Martin, Ber. 1909, 42, 3326; *see* also Grube, Zeitsch. Elektrochem. 1910, 16, 621).

Halogen compounds. Platinum monochloride PtCl has been obtained (Sonstadt, Chem. Soc. Proc. 1898, 25, 179).

Platinum dichloride or **platinous chloride** $PtCl_2$ is formed by heating chloroplatinic acid H_2PtCl_6 to 300°, or by heating spongy platinum in a current of dry chlorine at 240°–250° (Schützenberger, Ann. Chim. 1870, [iv.] 21, 351). It is a greenish-grey insoluble powder, sp.gr. 5·87, which readily decomposes on heating into its elements (Shenstone, Chem. Soc. Trans. 1892, 450).

It readily combines with phosphorus trichloride, forming the compounds $PtCl_2,PCl_3$, $PtCl_2(PCl_3)_2$, the aqueous solution of which, when evaporated *in vacuô*, form *chloroplatino phosphorous acid* $PtCl_2P(OH)_3$ and *chloroplatino diphosphorous acid* $PtCl_2,2P(OH)_3$ respectively. The latter is decomposed at 12°, forming the white crystalline compound $PtClOP_2(OH)_5$, which at 150° is converted into a yellow powder $PtClO_2P_2(OH)_3$ (Schützenberger, Bull. Soc. chim. 1872, [ii.] 17, 428; *ibid.* 18, 153; Rosenheim and Löwenstamm, Zeitsch. anorg. Chem. 1903, 37, 394).

Platinous chloride combines with carbon monoxide, forming a number of volatile carbonyl platinochlorides (Pullinger, Chem. Soc. Trans. 1891, 598).

Platinous chloride dissolves in hydrochloric acid, yielding platinochloric acid or chloroplatinous acid H_2PtCl_4, the potassium, other salts and compounds of which have been prepared (Thomsen, J. pr. Chem. 1877, [ii.] 15, 294; Nilson, *ibid.* 260; Magnus, Pogg. Ann. 1828, 14, 241; Klason, Ber. 1904, 37, 1360; Kurnakoff, J. Russ. Phys. Chem. Soc. 25, 565; Pigeon, Compt. rend. 1895, 120, 681).

Potassium chloroplatinite K_2PtCl_4 is the most important salt, owing to its use in photography (W. Willis, J. Soc. Chem. Ind. 1888, 7, 132). It is readily prepared by reduction of the chloroplatinite K_2PtCl_6 by $H_2S,SO_2,K_2C_2O_4,CuCl$ and other reagents. It crystallises well from water or KCl solution, but is insoluble in alcohol, as also is the ammonium salt.

K_2PtCl_4 is soluble in 108 parts of water at 16° and in 19 parts at 100°. It is less soluble in KCl solution.

$Na_2PtCl_4,4H_2O$ is efflorescent in dry air and extremely soluble in water (Nilson, J. pr. Chem. 1877, [ii.] 15, 260).

By reduction of sodium platinichloride with an excess of sodium hyposulphite a dark reddish-brown solution is obtained, which on evaporation yields a complex mixture of sodium platinosulphite compounds with $Na_2Pt_4S_6$. After filtration the solution first deposits crystals of sodium platinisulphite $Na_4[Pt(SO_3)_3(OH)_2],H_2O$ and then, on further evaporation, bright yellow crystals of sodium platinothiosulphate

$$Na_5[Pt(S_2O_3)_4],10H_2O$$

(Sailer, Zeitsch. anorg. Chem. 1921, 116, 209).

Platinum trichloride $PtCl_3$ has been obtained by Wöhler and Martin (*l.c.*) by heating platinic chloride in pure dry chlorine at 390° for 10 hours. It forms a dark green nearly black powder, soluble in boiling water, and decomposed by hot concentrated hydrochloric acid into the di- and tetra-chlorides.

Platinum tetrachloride or **platinic chloride** $PtCl_4$ is formed when platinum is heated in a current of chlorine (Troost and Hautefeuille, Compt. rend. 1887, 84, 946; Hodgkinson and Lowndes, Nature, May 3, 1888), or when dry chloroplatinic acid is heated in a current of chlorine or of hydrochloric acid (Pigeon, Compt. rend. 1890, 110, 77; *ibid.* 1891, 112, 1218; Ann. Chim. 1894, [vii.] 2, 433; Pullinger, *l.c.*). Hydrates containing 1, 4, 5, and 7 molecules of water have been prepared. In aqueous solution, the tetrachloride behaves as a weak dibasic acid $H_4PtCl_4(OH)_2$, and salts of this acid have been obtained (Miolati, Zeitsch. anorg. Chem. 1900, 22, 445; also Kohlrausch, Zeitsch. physikal. Chem. 1900, 33, 257; Hittorf and Salkowski, *ibid.* 1899, 28, 546; Dittenberger and Dietz, Ann. Chim. 1899, [ii.] 68, 853).

Platinichloric acid or **chloroplatinic acid** H_2PtCl_6 is prepared by dissolving platinum in *aqua regia* and evaporating with hydrochloric acid until all the nitric acid is removed. It may also be obtained by passing chlorine

through concentrated hydrochloric acid containing platinum black in suspension; or by the electrolysis in strong hydrochloric acid of platinum black as anode with platinum electrodes (Weber, J. Amer. Chem. Soc. 1908, 30, 29; *see* also Matignon, Compt. rend. 1902, 134, 1497).

It crystallises with 6 molecules of water and forms deliquescent prisms, orange-coloured if free from iridium. It readily yields crystalline salts of the type M'_2PtCl_6, known as the *platinichlorides* or *chloroplatinates*, of which the alkali salts are often used in analytical chemistry. It also forms characteristic salts with many organic compounds.

The sodium salt $Na_2PtCl_6,6H_2O$ crystallises well from water. The solution saturated at 15° has a sp.gr. 1·368 and contains 40 p.c. of anhydrous salt. The potassium and ammonium salts are anhydrous and form well-defined octahedra. 100 parts of water dissolve 0·926 part of K_2PtCl_6 at 15° and 5·26 parts at 100°, while for $(NH_4)_2PtCl_6$ the figures are 0·66 and 1·25 respectively (Crookes, Chem. News, 1864, 9, 37).

Archibald and Kern (Trans. Roy. Soc. Canada, 1917–1918, [iii.] 11, 7) find the following amounts dissolved by 100 grams of water at different temperatures:—

0·1	7·2°	18·0°	25·4°	29·9°
0·2902	0·3652	0·4869	0·5760	0·637
38·9°	49·7°	60·2°	70·0°	99·0°
0·787	1·0131	1·474	1·744	3·2515

Solutions of potassium platinichloride undergo hydrolysis when exposed to light (*cf.* Archibald, Chem. Soc. Trans. 1920, 117, 1104).

K_2PtCl_6 is much less soluble in KCl solution than in water, the figures at 20° in parts p.c. being

KCl . .	0·2	0·5	1	satd.
K_2PtCl_6 .	0·0236	0·0109	0·0046	0·0034

Similarly $(NH_4)_2PtCl_6$ is much less soluble in NH_4Cl solution than in pure water. The double aluminium chloride crystallises as

$$AlCl_3.PtCl_4,15H_2O$$

(Welkow and Schrauf. Ber. 1874, 7, 304).

A number of chloroplatinic acids and their salts intermediate between platinic acid $H_2[Pt(OH_6)]$ and the hexachloro acid have been described (Bellucci and Miolati, Atti R. Accad. Lincei, 1900, [v.] 9, ii. 51; *ibid.* 1902, [v.] 11, ii. 241, 271).

Platinous and platinic bromides and the corresponding acids (Meyer and Züblin, Ber. 1880, 13, 404; Halberstadt, *ibid.* 1884, 17, 2962; Bellucci Atti R. Accad. Lincei, 1900, v. 9, ii. 51), also the iodides and iodic acids (Bellucci, *ibid.* 11, i. 8; Pigeon, *l.c.*; Peterson, Zeitsch. anorg. Chem. 1898, 19, 59), the di-fluoride (Moissan, Compt. rend. 1889, 109, 807), and mixed halogen derivatives (Hertz, Ber. 1896, 29, 411) have also been prepared.

Potassium iodide forms a very delicate test for platinum. If excess of KI is added to a platinic solution free from nitric acid or excess of acid a deep red colour is produced. One part of platinum in 10,000 gives a rich rose, and one part in two million may be detected. Reducing agents immediately decolorise it, as also does warming.

Nitrogen compounds. A number of metallic *platino nitrites* or *nitrito platinites* and their oxalo- and other derivatives have been described (Lang, J. pr. Chem. 1861, 83, 415; Blomstrand, *ibid.* 1871, [ii.] 3, 207; Nilson, Ber. 1876, 9, 1722; *ibid.* 1877, 10, 934; Vézes, Compt. rend. 1891, 112, 616; *ibid.* 113, 696; *ibid.* 1897, 125, 525; Bull. Soc. chim. 1901, [iii.] 25, 157; *ibid.* 1902, [iii.] 27, 930; *ibid.* 1903, [iii.] 29, 83; Berg, Zeitsch. anorg. Chem. 1897, 15, 278).

Fulminating platinum $(OH)_5PtNH_3Pt(OH)_5$ strongly resembles ferric hydroxide in appearance. It is prepared by treating hexachlorplatinic acid with silver nitrate in the cold. The silver hexachlorplatinate so formed is decomposed with hot water, and the resulting tetrachlorplatinic acid again treated with silver nitrate, and the new silver salt decomposed by boiling with water for some hours. The following reactions take place:—

$$PtCl_6Ag_2+H_2O=Pt(OH)_2Cl_4H_2+2AgCl$$
$$Pt(OH)_2Cl_4Ag_2+H_2O=Pt(OH)_4Cl_2H_2+2AgCl$$

The solution of the dichloroplatinic acid treated with ammonia yields fulminating platinum, which when heated darkens, then detonates violently. A similar compound is obtained if pyridine is substituted for ammonia (Jacobsen, Compt. rend. 1909, 149, 574).

The various platinum salts form complex compounds with ammonia, similar in constitution to that of the chromium bases, and existing in two series in one of which the platinum is divalent, in the other tetravalent.

The chief types of platinous compounds are—

The platodiammines $[(NH_3)_4Pt]X_2$; platomonodiammines $[X(NH_3)_3Pt]X$; platosammine and platosemidiammine $[X_2(NH_3)_2Pt]$; and platosemiammine $[X_3(NH_3)Pt]R$. X and R= monovalent acid and basic radicles respectively.

The chief types of platinic compounds are represented by the following formulæ:—

$[(NH_3)_6Pt]X_4$;$[X_2(NH_3)_4Pt]X_2$;$[X_2(NH_3)_3Pt]X$; $[X_4(NH_3)_2Pt]$; $[X_5(NH_3)Pt]R$.

Magnus' green salt $Pt(NH_3)_4{\cdot}PtCl_4$, which was obtained by Magnus in 1828 (Pogg. Ann. 14, 204) by the action of ammonia on platinous chloride, is the starting-point for the preparation of all these derivatives. When boiled with ammonia it passes into *platodiammine chloride* or *tetrammine-platinous chloride* $[(NH_3)_4Pt]Cl_2$. The green salt may also be obtained by the action of potassium platinous chloride on platodiammine chloride, but if the solution is very dilute and neutral, or slightly ammoniacal, and traces of potassium platinichloride are absent, a rose-red crystalline salt is formed, which, when boiled with water passes into the green salt (Jörgensen and Sörensen, Zeitsch. anorg. Chem. 1906, 48, 441).

Literature.—Gras, Ann. Chim. [ii.] 69, 204; Peyronne, *ibid.* 1844, iii. 12, 193; 1846, [iii.] 16, 462; Reiset, *ibid.* 1844, [iii.] 11, 417; Compt. rend. 1844, 18, 1103; Schou, Zeitsch. anorg. Chem. 1896, 13, 36; Kurnakoff, *ibid.* 1898, 17, 207; Klason and Wauselin, J. pr. Chem. 1903, [ii.] 67, 41; Euler, *ibid.* 1904, 37, 2391; Tarugi, Gazz. chim. ital. 1906, 36, i. 364; Rây

and Ghosh, Zeitsch. anorg. Chem. 1909, 64, 184; Werner, Ber. 1907, 40, 4093; Jörgensen and Sörensen, *l.c.*; and many others). Organic derivatives of ammonia compounds have been described by Klason (J. pr. Chem. 1903, [ii.] 67, 1; Jörgensen, Zeitsch. anorg. Chem. 1906, 48, 374).

Platinum compounds of *hydroxylamine* have been described by Uhlenhuth (Annalen, 1900, 311, 120), and an explosive *potassium platino azoimide* by Curtius and Rissow (J. pr. Chem. 1898, [ii.] 58, 261).

Platinocyanic acid $H_2[Pt(CN)_4]$ is obtained by decomposing the copper or mercury salt with sulphurctted hydrogen or the barium salt with dilute sulphuric acid (Quadrat, Annalen, 1849, 70, 300; Weselsky, J. pr. Chem. 1856, 69, 276). When crystallising with 5 molecules of water it forms fine cinnabar-red prisms exhibiting a brilliant blue colour by reflected light; when containing more water the crystals have a yellow-green colour with a golden lustre. The crystals are deliquescent and very soluble in water, alcohol, and ether.

Platinocyanides may be prepared by dissolving well-washed freshly-prepared platinum sulphide in a solution of the corresponding cyanide. The colourless solution is then concentrated. The reaction proceeds thus:

$$PtS_2+5KCN=K_2Pt(CN)_4+K_2S+KCNS$$

(Schertel, Ber. 1896, 29, 204); or they may be prepared by double decomposition from the potassium salt which is formed by heating spongy platinum with potassium ferrocyanide to redness, or by dissolving platinous chloride in potassium cyanide (Knopp, Annalen, 1842, 43, 111.) The potassium salt is also formed by boiling platinum sponge in strong potassium cyanide solution. Hydrogen is evolved corresponding exactly with the amount of platinum dissolved (Deville and Debray, Compt. rend. 1876, 82, 241). This salt is also formed by the direct reaction of KCN and K_2PtCl_4 in solution, with considerable evolution of heat.

The barium salt $BaPt(CN)_4,4H_2O$ is soluble in 33 parts of water at 16°; insoluble in alcohol. The green fluorescent modification is best obtained from the yellow variety by recrystallising from water containing barium cyanide or baryta.

The magnesium salt $MgPt(CN)_4\cdot 7H_2O$ is characterised by a vivid dichroism. It is easily soluble in water, alcohol, and ether.

The platinocyanides are characterised by their reaction with the mercury salts with which they first give a white precipitate, which on addition of more mercury salt turns blue. They become luminous when exposed to Röntgen rays, and are used for making screens for the detection of these rays.

Nearly all platinocyanides fluoresce to a marked degree, the colour and intensity of fluorescence depending on the character of the basic radicle, the state of hydration, the perfection of the crystalline forms, and in some cases on the mode of preparation. Certain of the platinocyanides exist in two modifications, having the same crystalline form, but, prepared by different methods, they show a difference in all their optical characteristics. It is remarkable that *uranyl* platinocyanide displays no fluorescence, although each of its constituents confers this property on most salts (Levy and Sisson, Chem. Soc. Trans. 1906, 125; Levy, *ibid.* 1908, 1446; also Jackson, *ibid.* 1896, 57; also Levy, Proc. Camb. Phil. Soc. 1908, 14, 378).

Some further literature, Bergsöe, Zeitsch. anorg. Chem. 1899, 19, 318; Brochet and Petit, Compt. rend. 1904, 138, 1095; Reynolds, Proc. Roy. Soc. 1909, 82, A, 380. Dicyanodiamidinium platinic chloride $(C_2H_6N_4O)_2PtCl_6$ is described by Grossmann and Schück (Ber. 1910, 43, 674).

For thiocyanates, *see* Buckton, Chem. Soc. Trans. 1855, 22; Miolati and Bellucci, Gazz. chim. ital. 1900, 30, ii. 588; Grossmann and Schück, Ber. 1906, 39, 1896.

Sulphur compounds. Platinum monosulphide PtS forms a green powder or glistening needles, prepared by heating platinum sponge with sulphur in a vacuous glass tube (Debray and Deville, Compt. rend. 1879, 89, 587).

Platinum disulphide PtS_2 may be obtained pure as a steel-grey powder by precipitating a 3 p.c. solution of potassium platinichloride at 90° with sulphuretted hydrogen. At ordinary temperature, a yellowish-brown precipitate is formed, while the liquid becomes red, containing colloidal platinum sulphide, which is deposited at 0° (Antony and Lucchesi, Gazz. chim. ital. 1896, 26, i. 211).

Platinic sulphate $Pt(SO_4)_2,4H_2O$ forms large orange leaflets (Stuchlik, Ber. 1904, 38, 2913).

A number of *thio* platinum salts have been prepared (Schneider, Pogg. Ann. 1866, 138, 604; J. pr. Chem. [ii.] 48, 411; Hofmann and Höchtlen, Ber. 1903, 36, 3090). *Tellurides* Pt_2Te, $PtTe_2$, PtTe (Roessler, Zeitsch. anorg. Chem. 1897, 15, 405), and *selenides* PtSe, $PtSe_2$, $PtSe_3$ (Roessler, *ibid.* 1895, 9, 59; Minozzi, Atti R. Accad. Lincei, 1909, v. 18, ii. 150) also exist.

A platinum compound analogous to purple of Cassius (*v.* GOLD PURPLE) is obtained by the action of stannous chloride on solutions of platinum salts, when a blood-red solution is formed, which darkens after a time, particularly on warming, finally becoming black and slightly turbid. When shaken with ether or ethyl acetate the red colour is extracted, and on addition of water, a chocolate-brown precipitate is formed, consisting of platinum, tin, and oxygen in varying proportions. When freshly precipitated it is soluble in hydrochloric acid. It does not diffuse through parchment paper, and may be regarded as an adsorption compound of colloidal platinum and colloidal stannic acid, but the former shows none of the ordinary reactions of colloidal platinum. A similar red solution has been obtained by reducing platinic chloride with an ethereal solution of phosphorus in the presence of gelatin (Wöhler, Verh. deut. Naturforch. Aerzte, 1907, ii. 105; Wöhler and Spengel, Zeitsch. Chem. Ind. Kolloide, 1910, 7, 243).

Platinum phosphides PtP_2, Pt_3P_5 (Granger, Compt. rend. 1896, 123, 1284), **platinic pyrophosphate** PtP_2O_7 (Barnett, Chem. Soc. Trans. 1895, 513), *arsenides* $PtAs_2$ and the *arsenite* $Pt_3(AsO_3)_4$ (Stavenhagen, J. pr. Chem. 1895, [ii.] 51, 1); the *silicides* SiPt, $SiPt_2$ (Vigouroux, Compt. rend. 1896, 123, 115; *ibid.* 1907, 145, 376); and also *tungstates* and *molybdates* of

platinum (Gibbs, Amer. Chem. J. 1895, 17, 73) have been prepared.

Organic compounds of platinum. Alkyl compounds of platinum may be prepared by the interaction of magnesium methyl iodide and platinic chloride, a number of these substances and their hydroxide, nitrate, sulphate, chloride, cyanide, and platinocyanide derivatives have been prepared by Pope and Peachy (Chem. Soc. Trans. 1909, 571).

Platinous xanthate $(OEt{\cdot}CS{\cdot}S)_2Pt$ occurs in flat yellow prisms, m.p. 129°–130°, is insoluble in water, but readily soluble in chloroform.

Other platinous salts of thio-organic acids are described by Ramberg (Zeitsch. anorg. Chem. 1906, 50, 439).

Hydroxylamine platinum bases have been described by Lossen (Annalen, 1871, 160, 242); Alexander (*ibid.* 1893, 246, 239); Ulenhuth. *ibid.* 1900, 311, 120); Tschugaev and Tschernjaev (Chem. Soc. Trans. 1918, 113, 884).

Complex *platino pyridine halides* are described by Jörgensen and Werner, *ibid.* 1896, 12, 46; *ibid.* 1900, 25, 353; Klason, Ber. 1904, 37, 1349.

Organic phosphorus platino halides by Rosenheim and Levy (Zeitsch. anorg. Chem. 1905, 43, 34).

Platinum alginate is a brown gelatinous precipitate readily soluble in ammonia, forming a yellow solution (Stanford, J. Soc. Chem. Ind. 1886, 220).

For certain other organic compounds, *see* Werner, *l.c.*; Corsa, Gazz. chim. ital. 22, ii. 620; Hofmann and Rabe, Zeitsch. anorg. Chem. 1897, 14, 293; Prandtl and Hofmann, Ber. 1900, 33, 2981; H. and Bugge, *ibid.* 1908, 41, 312; H. and Narbutt, *ibid.* 1625; H. and Buchner, *ibid.* 1909, 42, 3392; Tschugaeff and Sokoloff, *ibid.* 55; Ostromisslensky and Bergmann, *ibid.* 1910, 43, 2768.

The preparation and catalytic properties of colloidal platinum have been the subject of a good deal of research of late years, chiefly in connection with the hydrogenation of unsaturated organic compounds. Many of the papers mentioned below refer also to colloidal palladium, similarly a very active catalyst. The protective colloids necessary for the stabilisation and separation of the metallic solvents are also referred to. Pappada, Zeitsch. Chem. Ind. Koll. 1911, 9, 270; Sieverts, *ibid.* 1913, 12, 263; Stark, Ber. 1913, 46, 2335; Amberger, Koll. Zeitsch. 1913, 13, 310; Skita and Meyer, Ber. 1912, 45, 3379; Paal and Windisch, *ibid.* 1913, 46, 4010; *ibid.* 1915, 48, 1195 and 1202; also J. pr. Chem. 1916, 93, 106; Spear and Kahn, J. Amer. Chem. Soc. 1918, 40, 181; Gutbier and Wagner, Koll. Zeitsch. 1916, 19, 280.

On the catalytic activity of *platinum black*, *see* Willstätter and Mayer, Ber. 1908, 41, 1475 and 2199: Vavon, Compt. rend. 1914, 158, 409; Lemoine, *ibid.* 1916, 162, 657; Cusmans, Atti R. Accad. Lincei, 1917, [v.] 26, ii. 87, and J. Soc. Chem. Ind. 1917, 112 (2), 641; Willstätter and Waldschmidt-Leitz, Ber. 1921, 54, [B], 113.

A. J. W.

PLECAVOL. Trade name for a mixture of cresols and formaldehyde.

PLUM, *Prunus spp.* Many species and varieties are known. As the average of 33 analyses, König gives for the composition of the fruit—

Water	Protein	Free acid (Malic)	Sugar	Other N-free ext.	Fibre and stone	Ash
78·6	1·0	0·8	8·8	4·0	5·8	0·5

For analyses of Californian-grown plums and prunes *v.* Colby (Experim. Stat. Rec. 1893, 4, 918), who found the juice of plums to contain about 18 p.c. of sugar and 0·5 p.c. free acid (as H_2SO_4).

The kernel contains amygdalin and emulsin; it is also rich in a fixed oil. For a determination of the amounts of oil and amygdalin in the plum kernel *v.* Kassner and Eckelmann (Arch. Pharm. 1914, 252, 402). The rind contains a wax melting at 64° (Seifert, Landw. Versuchs. Stat. 1894, 45, 29). Plums require and remove from the soil far larger quantities of nitrogen than are demanded by most other orchard crops, *e.g.* apples or pears. According to American estimates, an average crop of plums (30,000 lbs. per acre), removes about 127 lbs. of nitrogen, 13 lbs. phosphoric acid, and 51 lbs. of potash per acre from the soil, while for apples and pears (each 20,000 lbs. per acre), the figures are 12 and 12 lbs. of nitrogen, 6 and 10 lbs. phosphoric acid, and 16 and 36 lbs. potash respectively.

For effect of manuring upon the yield of plums and damsons *v.* Dyer and Shirvell (Jour. Roy. Hort. Soc. 1903, 27, part 4). H. I.

PLUMBAGO *v.* GRAPHITE.

PLUMBOJAROSITE *v.* JAROSITE.

PLUMIERIDE *v.* AGONIADA BARK.

PLUMOSITE *v.* FEATHER-ORE.

PNEUMIN. Trade name for a condensation product of creosote and formaldehyde.

PNEUMOSAN. Trade name for amylthiotrimethylamine.

PODOPHYLLIC ACID, PODOPHYLLOQUERCETIN, and **PODOPHYLLOTOXIN** *v. Podophyllum resin*, art. RESINS.

PODOPHYLLUM EMODI. *P. emodi* is a small herbaceous plant growing abundantly in Northern India. The root, or rather the rhizome, is employed medicinally in India as a powerful purgative, just, indeed, as the allied *P. peltatum* is used in Europe and America.

An examination of this root by Dunstan and Henry (Chem. Soc. Trans. 1898, 73, 209) has shown that in addition to *podophyllotoxin*, the active constituent, a considerable quantity of *quercetin* is present. According to Hummel this material in dyeing property compares favourably with quercitron bark, and should prove commercially valuable as a dyestuff at least to the native dyer. A. G. P.

PODOPHYLLUM RESIN *v.* RESINS.

POLARIMETRY.

I. QUALITATIVE.

When a ray of light falls on the surface of an isotropic substance like glass, it is, in general, bent out of its path at the surface of separation of the two media, according to a law discovered by Snellius about 1621. The incident and refracted rays lie in the same plane with the normal to the surface at the point of incidence, the sine of the angle of incidence divided by the sine of the angle of refraction being a constant.

In 1669, Bartholinus noticed that if a ray of light enters a crystal of Iceland spar, it splits

usually, into two rays, one of which pursues its way through the crystal according to the ordinary laws of refraction, whilst the behaviour of the other depends upon the direction of the original beam relative to the crystal face. The fundamental form of Iceland spar is the rhombohedron, Fig. 1, and if the edges of the rhomb be equal, the line joining the obtuse solid angles is the crystallographic axis. If the rhomb be not equal edged, the axis is any line parallel to this direction.

If a mark on white paper be examined through a crystal of Iceland spar, whose refracting face is parallel with the paper, two images will be seen. On turning the crystal about a vertical axis, one of these remains fixed whilst the other moves round it, a line joining the two images being always in the direction of the shorter diagonal of the face of an equal-edged crystal. The plane passing through this direction perpendicular to the face of the crystal contains the optic axis and is called the principal plane, the images being termed, respectively, ordinary and extraordinary. A ray incident on a surface cut parallel to the optic axis splits into two rays, each following the laws of single refraction but with a different refractive index, and when the ray is incident normally to the surface, the two rays coincide in direction but move through the crystal with velocities inversely proportional to their refractive indices, $\mu_o=1{\cdot}654$, $\mu_e=1{\cdot}483$.[1] Generally, however, the extraordinary ray is neither in the same plane with the normal and the incident ray, nor is $\frac{\sin i}{\sin r}$=a constant. If the crystal in the above experiment be tilted at different angles, it will be noticed that the separation of the images varies, and when the light travels through the crystal in the direction of the optic axis there is again no separation, both rays pursue the same path with exactly the same velocity.

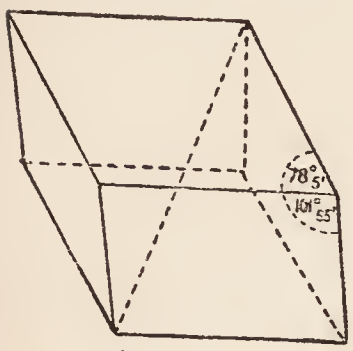


FIG. 1.

The theory of the propagation of these two wave-fronts was developed by Huygens, who discovered (1690) that both rays differ markedly from the original beam, for, if passed into another crystal situated similarly to that in which they were produced, they are not further resolved, the ordinary ray passes through as an ordinary, and the extraordinary as an extraordinary ray. If, however, their refracting faces being kept parallel, one crystal be turned through an angle of 90° relative to the other, the ordinary ray from the first passes through the second as an extraordinary and the extraordinary as an ordinary ray. In intermediate positions both rays are divided. Newton suggested that these rays have 'sides' (Optics, 1717, Queries 25, 26), meaning thereby that their properties vary in different directions, but the matter attracted little or no attention until after the lapse of another century, when Malus discovered, in 1808, that light could be brought into this peculiar condition by reflection as well as by refraction (Nouv. Bull. Soc. Philom. 1807–9, 1, 266, 341, 353; 1810–11, 2, 252, 291, 320; Gilbert's Ann. 1812, 40, 119, 132).

If a beam of light fall upon a sheet of glass, an angle of incidence of about 55° 25′ [1] giving the maximum effect, part will be reflected and part refracted. Both rays are found to have 'poles,' as Malus put it, and, if allowed to traverse a piece of Iceland spar, whose refracting face is perpendicular to the plane of incidence and whose principal plane is parallel to the plane of incidence, the reflected beam will pass through as an ordinary ray. The refracted ray under these circumstances will pass through as an extraordinary ray. The plane of incidence of the light on the reflecting surface came to be called the *plane of polarisation*.

The theory of the subject is due to Fresnel who, in connection with the phenomena of interference which had been discovered by Young, had just developed the transverse wave theory of light. He explained the difference between the ordinary and the extraordinary rays in Iceland spar by the supposition that, whilst the vibrations of the ether particles causing the ordinary ray take place in one particular plane, those causing the extraordinary ray occur in a plane at right angles to the first, and he thought that, on his hypothesis, the vibrations of light reflected from a surface at the polarising angle take place in a plane parallel to the surface and therefore at right angles to what was called the plane of polarisation (Nouv. Bull. Soc. Philom. 1824, 9, 150; Ann. Chim. 1821, 17, 186).

According to the modern electro-magnetic theory of light as developed by Clerk Maxwell, there is a magnetic disturbance *in* the plane of polarisation and an electric disturbance *perpendicular* to it. The latter, therefore, corresponds to Fresnel's vibrations.

In 1811, Arago discovered the phenomenon of the rotation of the plane of polarisation of light (Nouv. Bull. Soc. Philom. 1810–1811, 2, 358, 371, 387; Gilb. Ann. 1812, 40, 145). A ray reflected from a piece of glass at the proper angle is received upon a crystal of Iceland spar. It then splits in general into two rays of unequal intensity and, if the crystal be turned round the direction of the ray as axis, four positions will be found, at right angles, in which only one image appears, alternately ordinary and extraordinary. When the crystal is set in one of these positions, and a piece of quartz, cut perpendicular to the axis AA′ (Fig. 2), is placed in the path of the ray between the polarising mirror and the crystal, two images appear, complementary in colour—the colours depending on the thickness of the plate—and, if they happen to overlap, the part common to both is white. On turning the crystal the colours change. Something of a similar kind was found for mica and gypsum.

Arago recognised that passage through the quartz plate altered the plane in which the light was polarised, and that the colours were due to the fact that the planes of polarisation of the

[1] The double refraction of Iceland spar is said to be negative. The double refraction of quartz is positive, the indices being $\mu_o=1{\cdot}544$, $\mu_e=1{\cdot}553$.

[1] The angle varies with the index of refraction of the glass.

different rays of which white light is composed, are rotated to different extents.

Biot then found (Mém. de l'Institut, 1812, Part I. 218) that the rotation conferred on the plane of polarisation was proportional to the thickness of the plate, and varied with the refrangibility of the light used, the red rays being least rotated and the violet the most, some crystals rotating to the right, others to the left. Later, while engaged on experiments which necessitated the immersion of crystalline plates in liquids to make the polarised rays penetrate the plates very obliquely to the surface, he discovered some of these liquids also to be capable of rotating the plane of polarisation of light (Nouv. Bull. Soc. Philom. 1814–15, 4, 190). This was the case for oil of terebenthine (*l*-pinene, French oil of turpentine) and oil of laurel, each of which always turned the plane of polarisation from right to left, whilst oil of citron, and camphor dissolved in alcohol had the opposite effect. Experiments of a somewhat similar character were carried out by Brewster from about 1812, *e.g.* Phil. Trans. 1815, [i.] 29, and T. J. Seebeck (Schweigger's Journal, 1813, 7, 259, 382; 1814, 12, 1; Nouv. Bull. Soc. Philom. 1816, 5, 49). Subsequently Biot determined the effect of temperature change on the rotation of oil of terebenthine, examined the influence of solvents, discovered the rotation of cane sugar, applied the polarimetric method to distinguish between natural and artificial camphor and even ascertained that oil of terebenthine in the state of vapour, still retains its rotation [1] (Ann. Chim. 1818, [ii.] 9, 377; 1819, [ii.] 10, 68).

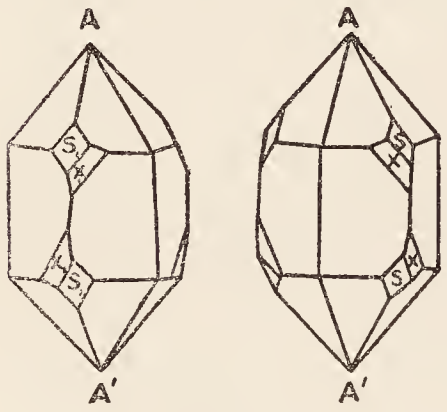


FIG 2.

Fresnel, after discovering circularly polarised light, showed that the rotation of the plane of polarisation of light by quartz cut perpendicular to the axis, could be explained, if on entering the quartz the polarised beam were resolved into two circularly polarised rays travelling through the crystal in the direction of the optic axis, without separation but with different velocities. Then, on emergence, there would be a difference of phase so that the two waves recombine to form again a plane polarised ray whose plane of polarisation is, in general, not that of the original beam. He succeeded in demonstrating the actual existence of these two circularly polarised rays, the principle of his method, if not the actual arrangement of his apparatus, being represented by Fig. 3. ABC and CDE are prisms of lævo- and BCD one of dextro- quartz, so cut that the optic axis of each is parallel to BD. Now let a ray of plane polarised light [2] fall normally on the surface AB at F, and suppose that it splits into two circularly polarised rays which travel in the direction FG. That ray whose path is a right-handed helix should travel with a greater velocity in the lævo prisms ABC and CDE than in the dextro prism BCD. In passing through the system, therefore, this ray should be bent towards the normal at G, and away from it at M and also at N. Similarly, the ray whose path is a left-handed helix should travel more slowly in ABC and CDE than in BCD and be bent away from the normal at G, towards it at H, and away from it at K. The two rays therefore emerge in the directions NO and KL. This separation was actually observed, although it was very small, and the two rays were found to be circularly polarised in opposite senses (Ann. Chim. 1825, 25, 147). Fresnel explained the rotation of liquids in the same way, but the experimental demonstration was made much later by v. Fleischl, whose method was similar to that of Fresnel, dextro- and lævo-rotatory liquids of the same refractive index being placed alternately in hollow glass prisms (Sitzungsber. Wien. Akad. 1884, 90, ii. 478).

Although Biot had found that some quartz crystals are dextro- and others lævo-rotatory, he was unable to suggest any property of the quartz—instancing crystalline form—which could be correlated with the phenomenon of rotation, but Herschel (Trans. Camb. Phil. Soc. 1821, 1 [i.] 43), remarking that the experiments

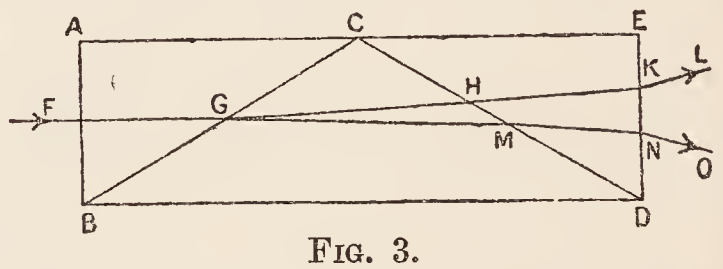


FIG. 3.

of Biot gave the impression 'of a want of symmetry in the disposition within the molecules themselves, of some of the elementary forces by which they act on light' (p. 43), pointed out that an indication of this want of symmetry had already been discovered by Haüy in the plagiehedrism or hemihedrism which shows itself in quartz by the presence of the little facets marked x and x′ in Fig. 2,[1] which in some crystals lean towards the right and in others towards the left. Plates cut from a crystal showing facets leaning towards the left, all rotated the plane of polarisation 'to the left, to an observer looking in the direction of the ray's progressive motion, or to the right of one receiving the ray in his eye' (p. 48). At the present time it is conventional to define the sign of rotation in the latter way so that his specimen was what is now called dextro-rotatory. In every other crystal examined the rotation was in the sense that would be expected from the position of the facets.

Some twenty years later, Louis Pasteur repeated, for practice in crystallography, a research published by de la Provostaye (Ann. Chim. 1841, [iii.] 3, 129) on the crystal forms of tartaric acid, paratartaric acid (racemic acid), and their salts, in regard to which it had been observed by Biot that tartaric acid is optically active (Mém. de l'Acad. 1835, 13, 46)

[1] It may be mentioned here that if the ray be reflected back through the tube of active substance, the rotation conferred on the plane of polarisation during the first passage is annulled during the second, the light emerging polarised in the original plane. *Cf.* p. 362.

[2] Ordinary light gives the same result.

[1] The figure given by Herschel represents a lævo twin crystal.

whilst racemic acid is inactive (Ann. Chim. 1838, [ii.] 69, 22). In this work (*ibid.* 1848 [iii.] 24, 442) he noticed something overlooked by de la Provostaye, namely that all the tartrate crystals had hemihedral facets, although they were not always very distinct, whereas racemic acid and such of its salts as he examined showed no hemihedrism. He also observed that the ratio of two of the axes in the tartrates is nearly the same, whilst the third differs considerably, and, if crystals of different tartrates be similarly situated, the arrangement of the hemihedral facets is always in the same sense. It may then have occurred to him that the relationship which had been inferred by Herschel for quartz might also apply in the case of the tartrates. Just about this time, Mitscherlich stated that: 'Sodium ammonium tartrate and sodium ammonium racemate have the same chemical constitution, the same crystal form with the same angles, the same specific gravity, and the same double refraction, in consequence of which their optic axes are inclined at the same angle; . . . the nature and number of the atoms, their arrangement and their distance from each other are the same in both compounds,' and yet tartaric acid in solution rotates the plane of polarisation of light whilst dissolved racemic acid is indifferent (Monatsber. der Berl. Akad. 1842; Compt. rend. 1844, 19,

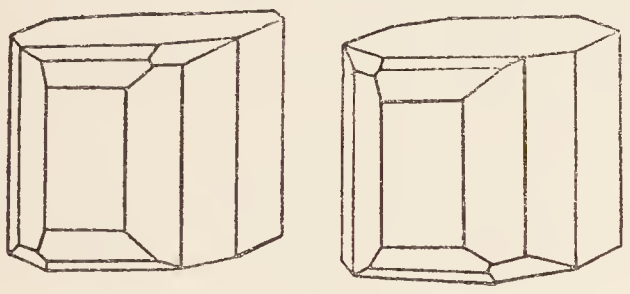


Fig. 4.

720). Pasteur, thinking it possible that Mitscherlich, like de la Provostaye, had overlooked the presence of hemihedral facets which might be expected on the tartrate but not on the racemate, then investigated these salts, which were not among those he had already examined. As he expected, the tartrate was indeed hemihedral, but, to his surprise, the racemate was hemihedral also. On closer examination, however, he noticed that whereas the facets on the tartrate crystals all occurred in the same position, in the racemate they appeared, sometimes towards the right, sometimes towards the left. Possibly still guided by Herschel's idea, he picked out from the mass some of each kind of crystal, and when dissolved separately in water one sort gave a dextro-rotatory and the other a lævo-rotatory solution. Fig. 4 shows the appearance of these crystals whose formula is

$$Na(NH_4)C_4H_4O_6,4H_2O$$

Racemic acid thus appeared as a compound or a mixture of a peculiar kind perhaps, of ordinary tartaric acid with another variety of tartaric acid, similar in every respect except its rotation and the shape of its crystals, which were exactly equal although opposite in sense. Racemic acid, however, does not separate, under any conditions at present known, into the two different forms, and indeed it is only by crystallising it within narrow limits of temperature that sodium ammonium tartrate will separate from solution in the two different forms. Herschel had already a distinct idea of a relationship between asymmetrical crystal structure and optical rotation and the idea was much developed by Pasteur as regards the chemical molecule. He pointed out that many of the objects with which we are acquainted can be separated into two classes: those which are superposible on their mirror images and those which are not. Thus the human body as a whole and apart from minor irregularities, a straight stair, a regular tetrahedron, are identical with their mirror images. But the mirror image of a right hand or of a left hand, of a spiral stair, of an irregular tetrahedron, although each is similar to its object, is not superposible on it; cannot, in the language of Euclid, be similarly situated; the image of a right hand is a left hand. The molecules of the two forms of tartaric acid Pasteur supposed to differ in the same way; the image of a dextro-rotatory molecule is a lævo-rotatory molecule. They would not then be expected to vary in regard to symmetrical forces or properties; they would have the same solubility, the same density, the same amount of water of crystallisation—or lack of it—the same melting-point, the same strength, and in many of their reactions they would behave alike, with ethyl alcohol or sodium hydroxide, for example. But with respect to certain other forces, presumably unsymmetrical, they behave exactly in opposite senses—whilst one rotates the plane of polarisation of light by a definite amount in one direction, the other rotates it by just the same amount in the opposite direction.

Pasteur further foresaw that by combining each of a pair of enantiomorphously related molecules with one form of some other active molecule, figures should be obtained which would no longer be completely enantiomorphic. Thus, for instance, if a right-handed and a left-handed spiral of equal dimensions be each combined with a right-handed spiral of a different diameter, the two compound figures will not be enantiomorphously related. Compounds such as they may be supposed to represent, need not be expected to show an identical behaviour even towards symmetrical forces. They might not have the same melting-point, for instance, or the same solubility. This Pasteur found to be the case. He prepared cinchonicine hydrogen racemate, and on allowing the solution to evaporate, the acid salt of cinchonicine with lævo-tartaric acid separated first, afterwards the corresponding salt of cinchonicine with dextro-tartaric acid also crystallised out. The two were quite different in appearance, in solubility, in melting-point, and from them the two different acids could be obtained. Thus Pasteur introduced that method which, since his time, has been used more than any other for the resolution of substances similar in character to racemic acid.

Pasteur carried his investigation a step further. It was known that commercial calcium tartrate occasionally fermented, with the formation of various products. He imitated this fermentation, first with ammonium tartrate, which was destroyed, and then with ammonium racemate. In the latter case, the liquid, originally inactive, gradually became lævo-

rotatory, and from it could be obtained ultimately lævo-tartaric acid. The micro-organisms had destroyed the dextro-acid, leaving the lævo-isomeride behind. Here, again, Pasteur established another method of a general character for the resolution of substances of the type of racemic acid. (For a fuller account of these researches *see* Alembic Club Reprints, No. 14, W. F. Clay, Edinburgh ; also Pasteur Memorial Lecture, P.F. Frankland, Chem. Soc. Trans. 1897, 71, 683).

Even this brilliant work, however, supplied no criterion to decide which chemical compounds were similar in character to racemic acid, and might therefore be expected to yield dextro- and lævo- isomerides, whilst theoretical organic chemistry was not at that time sufficiently developed to render possible a correlation of rotatory power with the constitution of naturally occurring active substances. Some twenty years had to elapse before this could be accomplished, the work of Pasteur being the incentive to one attempt to overcome the difficulty; the investigations of Wislicenus on the various forms of lactic acid, and the speculations of Kekulé, having much to do with another.

As Wislicenus pointed out, the plane formulæ in use about 1870 were insufficient to explain the existence of the three known lactic acids, and he suggested that this subtle isomerism



Fig. 5.

might perhaps be represented by different spatial arrangement of the atoms of the molecules. Paralactic acid and fermentation lactic acid were probably only geometric isomerides (Ber. 1869, 2, 550, 620 ; Annalen, 1873, 67, 343).

In 1874, van 't Hoff (in a pamphlet) and Le Bel (Bull. Soc. chim. 1874, [ii.] 22, 337) published practically identical views, referring the asymmetry which Pasteur had attributed to the molecule of an active compound as a whole, to one or more of its carbon atoms. If a carbon atom be combined with four different atoms or groups, and it be assumed that the affinities of the carbon atom are directed towards the angles of a tetrahedron, it is possible to arrange the four groups in two different ways such that the mirror image of the one arrangement is identical with the other arrangement (Fig. 5). Further, such compounds as were known to be optically active, contained carbon atoms of the above character, whence it might be inferred that any inactive compound containing an asymmetric carbon atom should be capable of resolution into active isomerides.

This idea explained all that Pasteur had discovered about tartaric acid. The constitutional formulæ then coming into use, exhibited the presence of two asymmetric carbon atoms in the substance, and by combining two such atoms in different ways it was possible to account for all the existing isomerides. Thus, in Fig. 6, the grouping of the radicles about the upper carbon atom is the same as that about the lower one, and since both the radicles of which the molecule is composed are the same in configuration, the molecule should be active, say in a *dextro* sense. Fig. 7 shows a molecule composed of two radicles each of opposite asymmetry to those of Fig. 6, and should therefore represent *lævo*-tartaric acid. A mixture of equal numbers of these molecules will constitute racemic acid, which is capable of resolution into the two active forms, whilst, if two radicles of opposite asymmetry be combined, as in Fig. 8, the molecule obtained should be inactive, because the two parts of which it is composed tend to turn the plane of polarisation of light equally in opposite directions, and, at the same time, it should not be capable of resolution since all the molecules composing it are exactly the same. This is the *meso*-tartaric acid of Pasteur. The spirals drawn round the asymmetric atoms and passing through the groups always in the same sequence, help to show that the twist given to the plane of polarisation of light is in the same sense at whichever end of the molecules (Figs. 6 and 7)

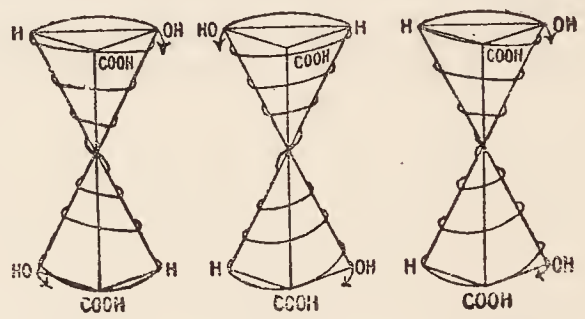
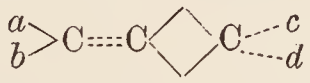


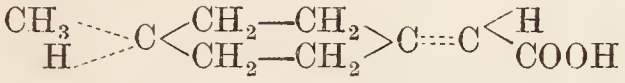
Fig. 6. Fig. 7. Fig. 8.

the ray enters. The lower formulæ of the Figs. 6, 7, 8, show the conventional method of projecting these three dimensional figures on to the plane of the paper.

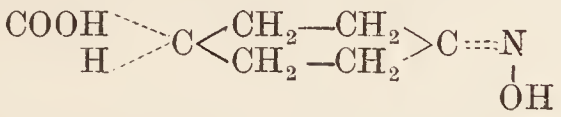
The work carried out on optical activity since the publication of the views of van 't Hoff and Le Bel has been, for the most part, a splendid confirmation of them, but, in some directions, there have been developments. It has been shown that carbon is not the only element that can give rise to optical activity. In the case of nitrogen, Pope and Peachey (Chem. Soc. Trans. 1899, 75, 1127) were successful in resolving benzylphenylallylmethylammonium iodide by means of *d*-camphorsulphonic acid (*see also* Pope and Read, *ibid.* 1912, 101, 519), and later, H. O. Jones (*ibid.* 1903, 83, 1418 ; 1904, 85, 223) resolved phenylbenzylethylmethylammonium iodide (*see also ibid.* 1906, 89, 280). Compounds owing their activity to the presence of an asymmetric tin atom were obtained by Pope and Peachey (Chem. Soc. Proc. 1900, 16, 12), others containing asymmetric sulphur by Pope and Peachey (Chem. Soc. Trans. 1900, 77, 1072), and Smiles (*ibid.* 1900, 77, 1174), asymmetric selenium by Pope and Neville (*ibid.* 1902, 81, 1552), asymmetric silicon by Kipping (*ibid.* 1907. 91, 209 ; 1908, 93, 2090), asymmetric

phosphorus by Meisenheimer and Lichtenstadt (Ber. 1911, 44, 356), and Kipping and Challenger (Chem. Soc. Trans. 1911, 99, 626), and even asymmetric cobalt (Ber. 1911, 44, 1887) and chromium (*ibid.* 1912, 45, 865) by Werner.

Pasteur attributed the rotation of chemical compounds to the asymmetry of the molecule as a whole and van 't Hoff pointed out, in 1877 (The Arrangement of Atoms in Space, 1898, 103), that a compound derived from allene of the formula  ought to exist in two enantiomorphic and therefore, active forms, because if *a*, *b*, and the bonds joining them to their carbon atom lie in the plane of the paper, *c*, *d*, and their bonds must lie in a plane perpendicular to the first, so that a tetrahedron could be laid through the points, *a*, *b*, *c*, *d*. Thus optical activity might exist in a compound containing no asymmetric carbon atom as defined by van 't Hoff. Attempts to prepare such substances failed until Perkin and Pope succeeded in synthesising *l*-methyl*cyclo*-hexylidene-4-acetic acid

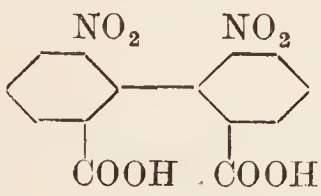


(which is not exactly of the above type) and this was later resolved into its two components by crystallisation of the brucine salt from dilute alcohol (Perkin, Pope and Wallach, Chem. Soc. Trans. 1909, 95, 1789; *see also* Perkin and Pope, *ibid.* 1911, 99, 1510). A compound the asymmetry of which is of the same kind is 4-oximino*cyclo*-hexanecarboxylic acid



(Mills and Bain, Chem. Soc. Trans. 1910, 97, 1866), but the claim that these compounds really contain no asymmetric carbon atom has been disputed by Everest (Chem. News, 1909, 100, 295; Chem. Soc. Proc. 1911, 27, 285), and Marsh (*ibid.* 1911, 27, 317; *see also* P. F. Frankland, Chem. Soc. Trans. 1912, 101, 655).

A further interesting development, the full significance of which is not yet apparent, is the separation of γ-6 : 6′ dinitrodiphenic acid,



into oppositely active components by Christie and Kenner (Chem. Soc. Trans. 1922, 121, 614).

Additional Methods for producing Optically Active Compounds.

To Pasteur's three methods for obtaining optically active compounds there may be added some others. Marckwald and McKenzie found (Ber. 1899, 32, 2130) that when mandelic acid was heated with menthol for an hour at 155°, the mandelic acid which remained unacted on, contained a greater proportion of the lævo- than of the dextro- constituent, and on this fact a method can be based for separating them. Something of a similar type to this, inasmuch as it would seem to depend upon a difference in velocity of reaction of a reagent upon an equimolecular mixture of partial stereoisomerides, has recently been reported by Shimomura and Cohen (Chem. Soc. Trans. 1921, 119, 1816).

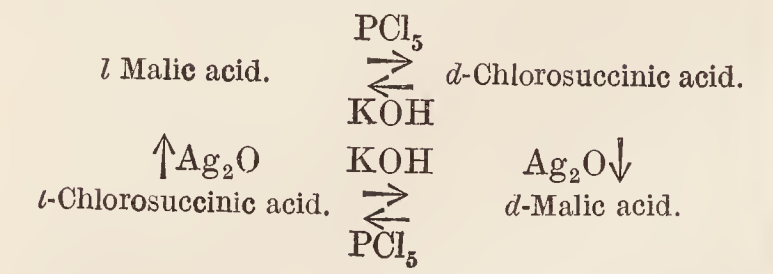
Again, when an inactive substance, while in combination with an active compound, is submitted to some reaction which produces in it an asymmetric carbon atom, it often happens that one arrangement of the groups around this new asymmetric atom is produced in preference to the other. The new asymmetric molecule can then be separated from the one originally active. Thus, for example, by reduction of *l*-menthyl pyruvate CH_3—CO—CO·$OC_{10}H_{19}$, *l*-menthyl lactate CH_3—CH(OH)—CO·$OC_{10}H_{19}$, was obtained (McKenzie, Chem. Soc. Trans. 1905, 87, 1373), and the lactic acid separated from this was found to be slightly lævo-rotatory. By such processes of *asymmetric synthesis*, McKenzie has produced other active compounds (*ibid.* 1904, 85, 1249; 1905, 87, 1004; 1906, 89, 365).

An ingenious asymmetric synthesis was also carried out by Marckwald, by heating the acid brucine salt of methyl-ethyl-malonic acid, when valeric acid was obtained containing a slight excess of the lævo-isomer (Ber. 1904, 37, 349, 1368). These methods are, meanwhile at least, only of theoretical interest.

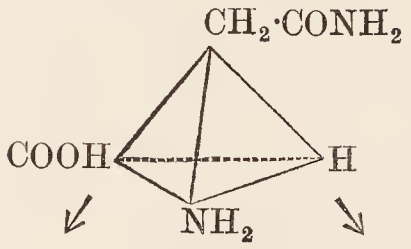
The 'Walden Inversion.'—Pasteur showed that *d*-tartaric acid can be converted into *l*-tartaric acid by an indirect process. By heating *d*-tartaric acid under certain circumstances (Pasteur, Compt. rend. 1853, 37, 162; Jungfleisch, Bull. Soc. chim. 1872, 18, 201; Winther, Zeitsch. physikal. Chem. 1906, 56, 466, 720), a rearrangement of the groups about the asymmetric atoms takes place and ultimately an inactive mixture of racemic acid and *meso*tartaric acid is obtained. The racemic acid can then be resolved by one or other of the processes he had discovered. It would be possible, theoretically, to transform practically the whole of a given quantity of *d*-tartaric acid into the lævo variety, but the experimental difficulties would be very great. Since the method proceeds by racemisation, the substance operated on passes through a stage of inactivity.

In certain cases, however, it is possible to transform a molecule of one asymmetry into a molecule of opposite asymmetry without passing through any stage of inactivity. *Lævo*rotatory asparagine when acted on by nitrous acid yields *lævo*rotatory malic acid, and Walden found that *l*-malic acid yielded with phosphorus pentachloride, a *dextro*rotatory chlorosuccinic acid, which therefore might be supposed to correspond in configuration to *l*-malic acid and to asparagine. Tilden and Marshall, however (Chem. Soc. Trans. 1895, 67, 494), observed that *lævo*rotatory asparagine gave with nitrosyl chlorine a *lævo*-rotatory chlorosuccinic acid; whilst Walden, about the same time, discovered (Ber. 1895, 28, 2769) that this asparagine treated directly with bromine and nitric oxide gave a *lævo*rotatory bromosuccinic acid. Thus, starting from *lævo*-rotatory asparagine, we can prepare according to the reagents used, either *lævo*rotatory or *dextro*rotatory chlorosuccinic acid.

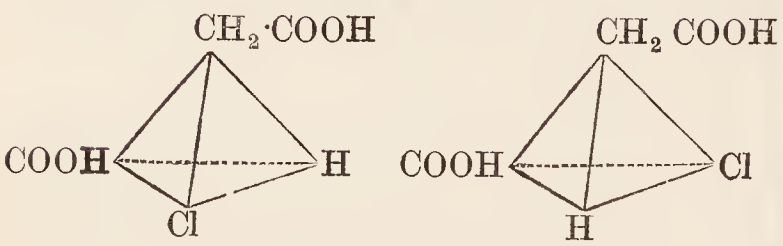
Later, Walden (Ber. 1896, 29, 133) completed the following cycle :—



in which caustic potash and silver oxide act on the chlorosuccinic acids in an exactly opposite manner. One of these changes must be abnormal and accompanied by an exchange of two of the radicles attached to the asymmetric carbon atom. In one case the NH_2 group of the asparagine is replaced directly ; in the other it, or the chlorine atom which is substituted for it, exchanges places at the same time with one of the other groups.



Asparagine.



Chlorosuccinic acid.

These reactions are generally accompanied by a little, and often by a great deal, of racemisation.

So far, little of a really general character has been discovered about this most interesting reaction. For further details the papers of Walden (Ber. 1899, 32, 1833), Fischer (*ibid.* 1907, 40, 489 ; 1908, 41, 889, 1286, 2891 ; Annalen, 1911, 381, 123), and McKenzie (Chem. Soc. Trans. 1908, 93, 811 ; 1910, 97, 2564, etc.) should be consulted in addition to those already mentioned. *See* also the Chemical Society's Annual Reports, and P. F. Frankland, Chem. Soc. Trans. 1912, 101, 672 ; 1913, 103, 713 ; Clough, *ibid.* 1918, 113, 526 ; and Walden's monograph on the reaction.

II. Apparatus.

The apparatus used by Biot (Ann. Chim. 1840, [ii.] 74, 428) and others consisted of a polarising mirror, the light from which, after passing through the substance under investigation, was examined by means of a double refracting rhomb of Iceland spar, or a prism such as that of Rochon or Wollaston, adjustment being made to those positions in which one or other of the images vanished.

A great improvement was made by Nicol (Edin. New. Phil. Jour. 1828, [ii.] 6, 83 ; 1831, [ii.] 14, 372 ; 1839, [ii.] 27, 332), who invented the prism bearing his name (Fig. 9). It is usually made from a rhomb of Iceland spar about three times as long as broad, and the end faces, ABCD and EFGH should first be ground down so as to reduce the acute angles EAC and CGE from 71° to 68°, but this seems seldom to be done (S. P. Thompson, Phil. Mag. 1886, [v.] 21, 479). The prism is then cut through in the plane EKCL perpendicular to the principal section, in this case the plane through ACGE. The plane EKCL[1] makes an angle of 90° with the faces ABCD and EFGH. The two halves of the prism are then cemented together again in their

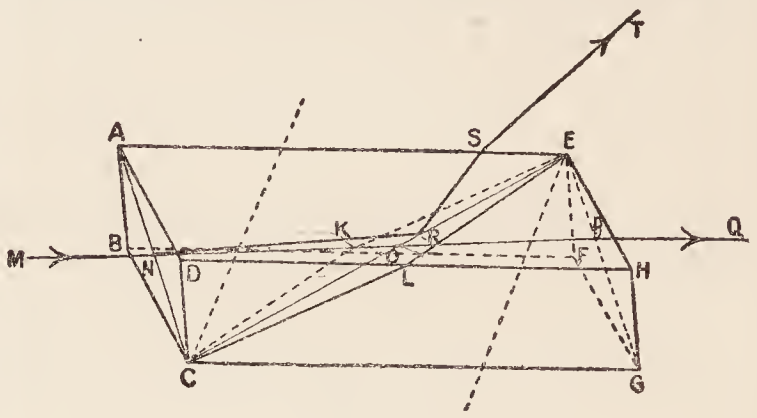


Fig. 9.

original position by means of Canada balsam or Copaiva balsam, the indices of refraction of which lie between those for the ordinary and the extraordinary rays. The index of refraction of the ordinary ray being 1·654 and that of Canada balsam 1·55, it can easily be shown that any ray whose angle of incidence on the plane of section is greater than 69·5°, will be reflected out of the prism. On looking through the prism and tilting it so as to allow the rays to fall very obliquely on the face ABCD, this limit is marked by a series of interference spectra.

The other limit is conditioned by the fact that whereas the index of refraction of the ordinary ray, 1·654, applies in any direction through the crystal, that for the extraordinary ray, 1·483, only holds perpendicular to the optic axis. As the direction of the ray through the crystal approaches more nearly to that of the optic axis, the value of μ_e approaches 1·654, and in some intermediate position will have the value 1·55, equal to that of the Canada balsam. All extraordinary rays having a value greater than this are liable, like the ordinary rays, to be totally reflected at the balsam film. Fig. 10 shows the prism in section through ACGE. All rays below WV—such that the angle VXC is about 10°—ordinary or extraordinary, suffer total reflection. On tilting the prism so that the rays fall almost

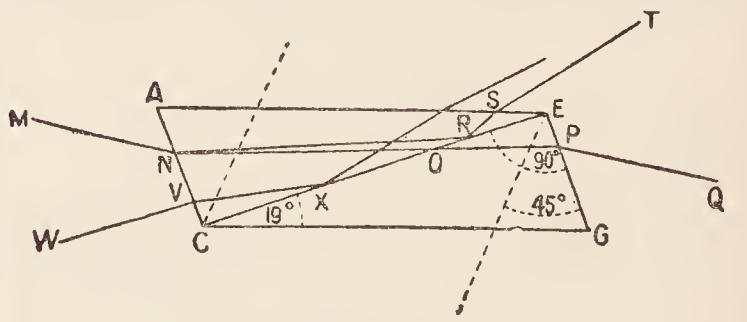


Fig. 10.

normally on the refracting face, this limit is marked by a broad blue and violet band. All

[1] It should be noted that the direction of the plane of section is practically immaterial ; all that is necessary is that it should make a suitable angle with the rays traversing the prism. If the plane were laid from D to F the ordinary rays, the vibrations of which are perpendicular to this plane, would be reflected out to the remote side of the prism, whilst the extraordinary rays would pass on as before.

rays, therefore, between MN and WV should be polarised in passing through the prism. The angle between these directions is some 32°.

The action of the prism does not depend on the *separation* of the two rays which occurs in the crystal. It is usually a cone of light that enters the prism so that ordinary and extraordinary rays may travel side by side, but on account of their different velocities in the crystal the former are totally reflected at the film whilst the latter pass through it. The vibrations constituting the ordinary ray are supposed to take place in a plane parallel to BD (Fig. 9), those of the extraordinary ray in one parallel to AC, and therefore they are polarised in planes at right angles to these.

Fig. 11 represents a Nicol prism, end on. The principal plane passes through AC perpendicular to the plane of the paper. If a source of light be examined through two Nicols placed one behind the other so that their principal planes coincide (Fig. 12), the vibrations which pass through EFGH—the remote prism, the polariser—and which are parallel to EG, will also pass through ABCD ; but when the prisms are crossed (Fig. 13) the light which passes through EFGH, vibrating parallel to EG, is stopped by the analyser, ABCD, so that part of the field appears dark.

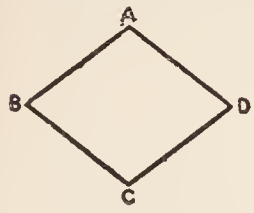


Fig. 11.

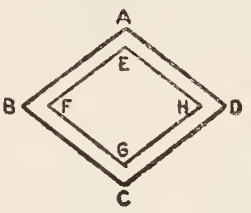


Fig. 12.

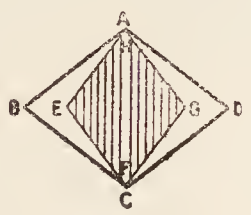


Fig. 13.

The Nicol prism, however, has several defects, one of these being the expense of large, clear pieces of spar. For this reason, Foucault (Compt. rend. 1857, 45, 238) invented a prism (Fig. 14) whose length is only about 1·25 times that of one of the sides of the refracting face, the plane of section making with the upper and lower edge an angle of 59°. The Canada balsam is replaced by air. An ordinary ray in the prism incident on this film at any angle greater than 37° 10′ will be totally reflected, the field being limited on this side by interference fringes ; an extraordinary ray incident on the film at any angle greater than 42° 20′ will also be totally reflected, the limiting position being marked by a broad red band. Between these angles ordinary rays will be totally reflected and extraordinary rays will pass through. The field of view is thus very narrow, only comprising for the rays before they enter the prism, some 8°.

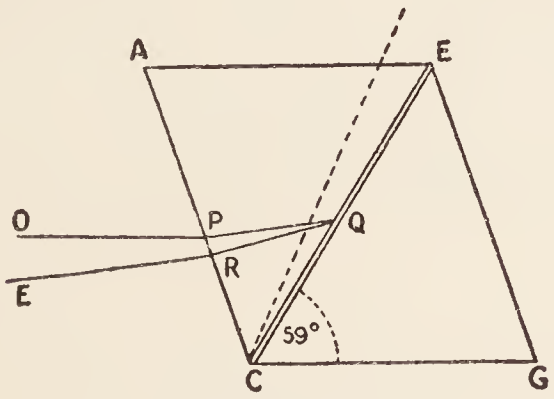
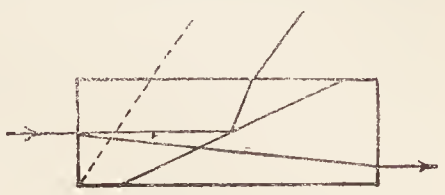
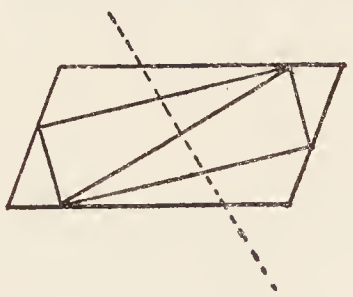


Fig. 14.

Again (1), part of the light incident on the sloping end face of a Nicol is reflected there, and (2) a ray of light falling on the prism in the direction of the axis of length, emerges parallel to its original direction but somewhat displaced, so that if the Nicol be rotated the image circles round the field, this being the case even if the ends of the prism are cut square, as shown in Fig. 15. The extraordinary ray will pass through the prism without displacement only if the refracting surface is cut parallel to the optic axis. A prism, cut as shown in Fig. 16, which partly corrects these faults, was first described by Hartnack and Prazmowski (Ann. Chim. 1866, [iv.] 7, 181). The end faces are still inclined at an angle to the axis, but the plane of section is perpendicular to the optic axis.


Fig. 15.


Fig. 16.

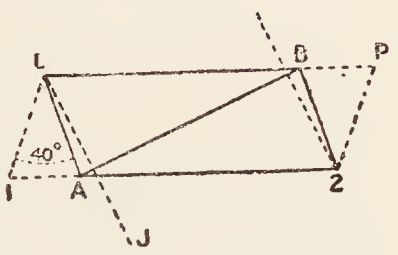


Fig. 17.

S. P. Thompson (Phil. Mag. 1886, [v.] 21, 478) modifies the Nicol prism so as to improve considerably its polarising properties. LIZP (Fig. 17) represents a section of a rhomb of spar, LJ being the direction of the optic axis. In an ordinary Nicol, the plane of section would pass from L to Z. The acute solid angles at I and P are cut off by the parallel planes LA, ZB, such that ILA=40° ; the plane of section AB is almost at right angles to LA and BZ. There is thus comparatively little loss of material, and since the rays travel through the prism nearly perpendicular to the optic axis, the blue band which marks the limit of the transmitted extraordinary waves is thrown back so that with a shorter prism a field of about 39° is obtained.

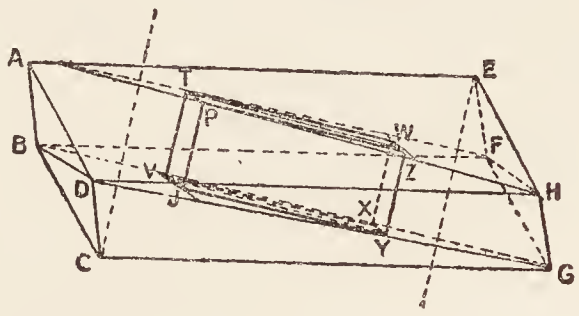


Fig. 18.

Other prisms, more or less alike, have been described by S. P. Thompson (Phil. Mag. 1881, [v.] 12, 349), R. T. Glazebrook (*ibid.* 1883, [v.] 15, 352), and P. Glan (Carl. Rep. 1880, 16, ii. 9, 570 ; Fortschr. d. Physik. 1880, [v.] 10, 247). Fig. 18 gives a rough idea of how this prism is situated relative to the original crystal. By planes perpendicular to the optic axis, the solid angles at C and E are first removed, the prism TVJP, WXYZ, being then cut out of the remaining spar. The plane of section is laid through TVZY.

The optic axis is thus parallel to the refracting faces, TVJP and WXYZ, whilst the balsam film lies in a principal plane of section, that is, is parallel to the optic axis. There is great waste of material in cutting this prism, but its angle of view is increased and the polarisation is almost perfect.

The prism (Fig. 19), described by Lippich (Wien. Sitzungsber. 1885, ii. 91, 1079; Beibl. Ann. d. Phys. 1887, 11, 455) for his polarimeter,

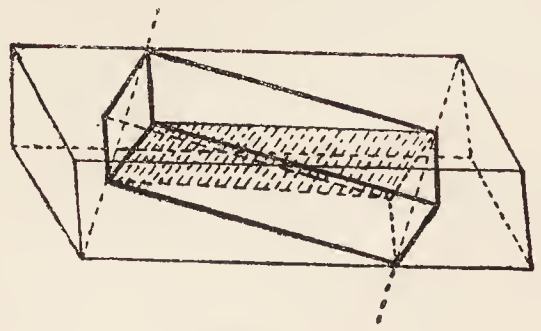


FIG. 19.

has straight end faces of square section and a linseed oil film. The optic axis is perpendicular to the axis of length: its position relative to the plane of section is immaterial.

Fig. 20 shows the modern form of Nicol prism. A ray of light falling normally on the refracting face does not separate into two rays pursuing distinct paths through the crystal, but at the balsam film the ordinary ray is reflected out whilst the extraordinary ray passes on without deviation. If the optic axis be parallel to the plane of section the prism is of the Glan-Thompson variety, whilst if it be perpendicular to the plane of section the prism is technically referred to as a Lippich Nicol, although this is not strictly in accordance with Lippich's own statement (*v. supra*). The two parts of the prism are usually cemented together with linseed oil, which is superior to Canada balsam, but takes a long time to dry.

A paper read by E. Sang before the Royal Society of Edinburgh in 1837, discussing the theory of the Nicol prism, is remarkable, partly because fifty-four years elapsed before it was published (Proc. Roy. Soc. Edin. 1891, 81, 323), but also because it contained the first suggestion for a different type of prism, one to transmit the ordinary and reflect out the extraordinary ray. A right prism of dense glass whose index of refraction is, preferably, just the same as that for the ordinary ray in Iceland spar, is cut through obliquely (Fig. 20 may be taken to illustrate this prism also) and a thin lamina of Iceland spar or sodium nitrate, cut parallel to the optic axis, is introduced between the two parts and brought into optical contact with the cut faces or joined to them by means of some cement with an index of 1·654 or higher. A beam of light passing from the glass to the spar separates into two rays. The ordinary ray, with the same index in the spar as in the glass, goes straight through. For the extraordinary ray, however, the index is much lower in the spar than in the glass and if the ray is incident on the layer of spar at an angle of 74° or more, it will not penetrate it at all. This idea was discovered also by Jamin (Compt. rend. 1869, 68, 221; Pogg. Ann. 1869, 137, 174), and a description of a prism on this principle was given by E. Bertrand (Compt. rend. 1884, 99, 538), which, by means of a double plane of section had a field view of 98°.[1]

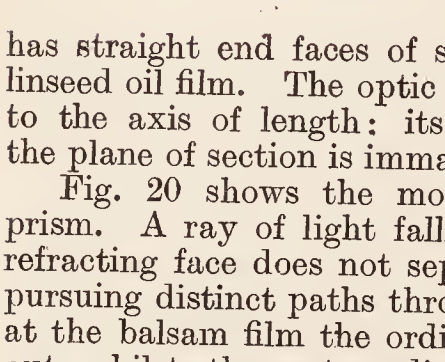


FIG. 20.

The Polarimeter.—Nicol's prism appears first to have been used in a polarimeter by Mitscherlich (Lehrbuch der Chemie, 4th ed. 1844, i. 361), whose instrument (Fig. 21) was fitted at one end with a Nicol prism beyond which a source of monochromatic light was placed. At the other end, another Nicol was fixed to a pointer which could be turned round over a graduated scale. The prisms were then set to the position of maximum darkness, which is the zero point of the instrument. If an active substance be interposed between the crossed Nicols the field will become more or less illuminated,

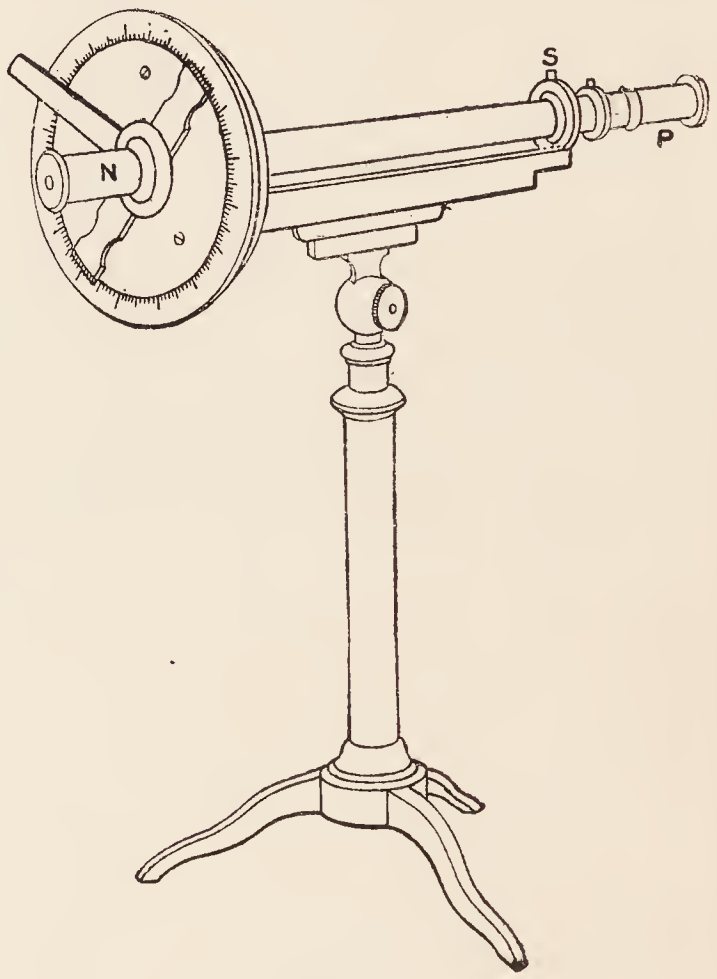


FIG. 21.

and in order again to reach the position of maximum darkness the analyser must be turned round either towards the right hand—at the top of the scale—clockwise, or towards the left hand. In the former case, the substance is dextrorotatory, in the latter, lævorotatory. Adjustment is always made for the position of maximum darkness, since about this point a small displacement of the prism makes a considerable difference to the eye. The position of maximum brightness is much more difficult, in fact impossible, to adjust to.

Suggestions to obtain greater sensitiveness were made by Robiquet and by Wild, whilst a very ingenious prism was invented by Jellett (Brit. Assoc. Rep. 1860, 29, 13), but perhaps the most commonly adopted proposal was that of Laurent (Journ. de Physique, 1874, iii. 183;

[1] An article 'On the Nicol Prism and its Modern Varieties,' by S. P. Thompson, containing a bibliography of the subject, will be found in the Proceedings of the Optical Convention, 1905, p. 216.

Dingl. poly. J. 1877, 223, 608). He placed between the polariser and the analyser, close to the former, a glass plate to which is cemented a half disc of quartz or gypsum cut parallel to the axis, called a half wave-length plate. The general arrangement is shown in Fig. 22. P is the polariser, generally a Foucault prism, D the glass plate partly covered by the quartz half

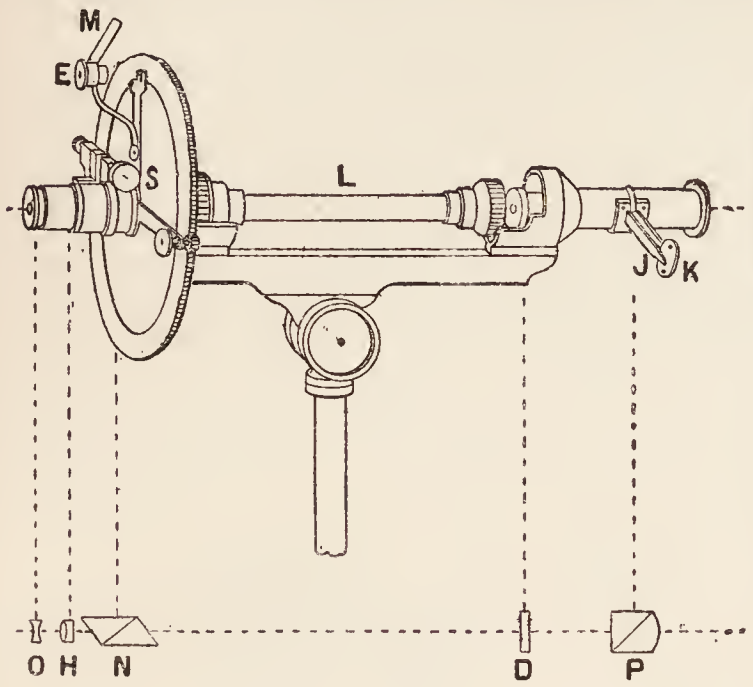


FIG. 22.

disc, N the analyser, usually a Nicol prism. The telescope OH is focussed on the straight edge of the quartz plate. In Fig. 23, let the circle FGKH represent the polariser diaphragm; FGK is the half disc of quartz whose optic axis may lie in any direction in the plane of the paper such as OB or DC or OG. Suppose that it is parallel to OC. The direction of vibration of light waves from the polariser, RSTU, passing through the diaphragm as seen end on, will be, for example, OA representing those falling on the glass plate, and DC, representing those falling on the quartz. The wave OA on its passage through the glass plate, may be regarded as resolved into two components, vibrating respectively parallel to OE and to OC. They travel with the same

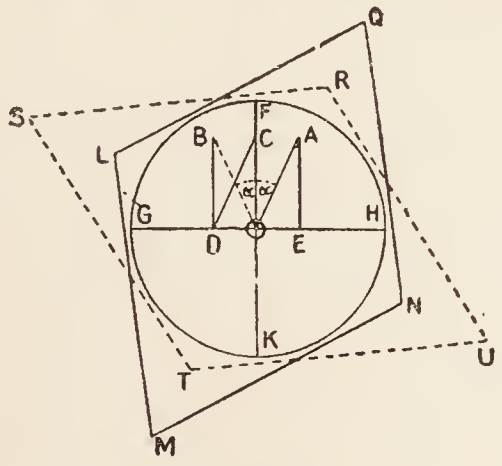


FIG. 23.

velocity and the same wave-length, the resultant being thus always parallel to OA. A wave falling on the quartz plate, however, like DC, is resolved into a component parallel to DO, the ordinary ray, and one parallel to OC, the extraordinary ray, these being in reality very narrow ellipses (Airy, Ed. Journ. Sci. 1831, 5, New Ser. 324; P. G. Tait, Light, 1889, p. 253; W. Voigt, Ann. d. Physik. 1905, [iv.] 18, 645). At the moment when the light touches the plate the particle of ether at D of the component DO is displaced towards O, and simultaneously the particle of ether at D of the component DB is displaced towards B, the resultant being in the direction DC. These component waves travel through the plate with different velocities, that of the ordinary ray, DO, being the greater in the ratio 1·553/1·544. After a certain short interval of time, therefore, the extraordinary ray will have fallen one half wave-length behind the ordinary ray. At this moment the vertical displacement is OC whilst the horizontal displacement is OD. The resultant is thus OB, the plane of vibration of the light having been turned through an angle 2α where α is the angle between the principal plane of the polariser and the optical axis of the quartz plate. As the two components proceed further into the quartz plate, the ordinary ray gains a whole wave-length which brings the resultant back into its original position parallel to DC. In pursuing its way through the quartz plate, the plane of vibration of the light thus oscillates between the directions DC and OB. The plate is made of such a thickness that, on emergence, the ordinary ray is one half wave-length ahead of the extraordinary ray for the kind of light used, and therefore the plane of vibration is parallel to OB. Whatever angle the original vibrations may make with OF, passage through the quartz plate inverts it symmetrically. The special character of this rotation of the plane of vibration of the incident light by the quartz plate should be carefully noticed. It is of an entirely different nature from the rotation which would be produced by a plate of quartz cut perpendicular to the axis.[1]

If now the light which has passed through the whole polariser system be examined by a Nicol prism, LMNQ, placed as shown in the figure, its principal plane at right angles to that of the polariser, the rays that have traversed the glass plate and vibrate parallel to AO will be stopped by the analyser and the half FHK of the circular field will appear dark. But those that have come through the quartz plate and are parallel to BO will pass to a considerable extent through the Nicol so that FGK will appear relatively bright. If the principal plane, LN, of the analyser be set perpendicular to BO, FGK will appear dark and FHK bright. Midway between these positions, the whole field should appear uniformly dark. If the analyser be turned through 90° so that its principal plane is parallel to the axis of the quartz plate the whole field should appear uniformly bright.

The accuracy of a setting depends on the size of the angle α. If it be small a very slight movement of the analyser should suffice sharply to reverse the relative brightness of the sides of the field. The milled head is then oscillated back and forward from a position of darkness on one side to a position of similar darkness, as judged by the eye, on the other, the oscillations being gradually narrowed down until the median position is reached. The angle α must not be made too small, however, as then the amount of light cut off is very great and the eye ceases to be able to distinguish clearly between the

[1] An instrument dependent on the action of a quartz plate cut perpendicular to the axis, or on a cell containing sugar solution, was suggested by J. H. Poynting (Phil. Mag. 1880, [v.] 10, 18).

brightness and darkness of the two halves of the field. The Laurent polarimeter can be used, of course, with only one kind of monochromatic light, being generally made for sodium light, which is purified by passage through a plate of potassium dichromate before entering the polarising system.

The Lippich polarising system is that most commonly used at the present time (Wien. Sitzungsber. 1885, ii. 91, 1079; 1895, ii. 105,

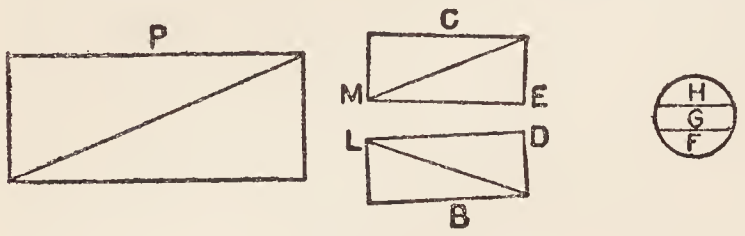


Fig. 24.

317). It is accurate, may be used with any kind of monochromatic light, and can be made to give a double or a triple field, the latter being the more delicate. Fig. 24 shows a plan of the arrangement. P is the polariser, just beyond which and taking the place of the quartz plate of the Laurent instrument, are two small prisms, each of the same depth but about one half the width of the polariser. For the small prisms both Hilger and Schmidt and Haensch use Lippich Nicols, whilst for the

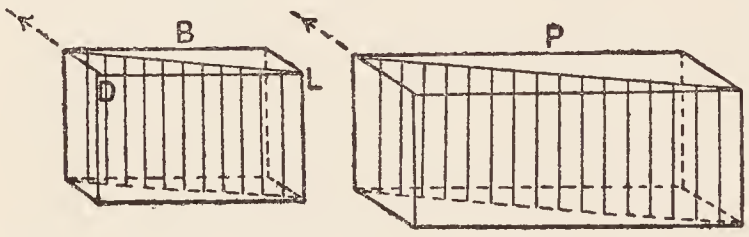


Fig. 25.

polariser Hilger uses a Lippich and Schmidt and Haesnch a Glan-Thompson Nicol. Figs. 25 and 26 represent these systems in perspective, one of the small prisms being omitted in each case. The direction of the optic axis is indicated by the dotted arrows. The polariser is rectangular, but the small prisms have an angle of about 93° at D and E and of about 87° at L and M (Fig. 24). The small prisms are fixed so that their faces LD and ME are inclined at a slight angle to the

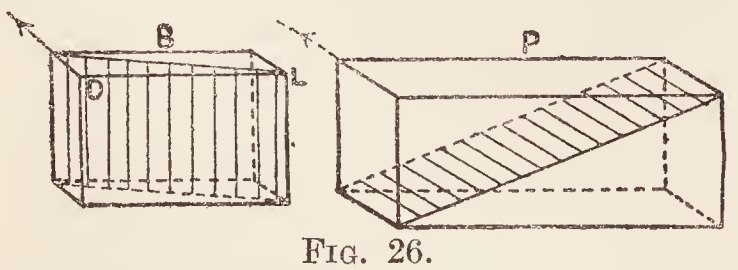


Fig. 26.

axis of the instrument, but the edges D and E are parallel or very nearly so. The eyepiece is focussed on these edges, which usually appear as faint lines dividing the field into three parts. Of these, F is illuminated by light which has passed through P and B; G by light which has passed through P only; and H by light which has passed through P and C. The polariser P is capable of rotation some 15° about the axis of the instrument, and in average work is placed so that its principal plane makes an angle of 2° to 5° with the principal planes of the small prisms. If now this system be viewed through the analyser with its principal plane placed perpendicularly to that of P, G should appear dark and F and H fairly bright. If the analyser be turned so that its principal plane is perpendicular to those of B and C, F and H should appear dark and G relatively bright. The analyser should then be oscillated about between these positions, the movements becoming smaller and smaller, until the final adjustment is reached.

Source of light.—The light commonly used for polarimetric purposes is that afforded by incandescent sodium chloride vapour (Fox Talbot, Phil. Mag. 1833, [iii.] 3, 35). Fig. 27 represents one lamp suitable for producing it and another is shown in Fig. 28. In the former, salt is placed in a little movable spoon which is then swung into the flame; in the latter, a large

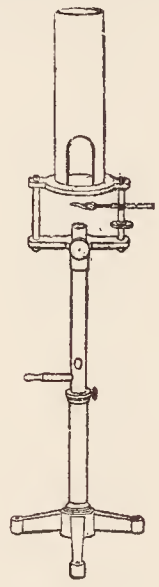


Fig. 27.

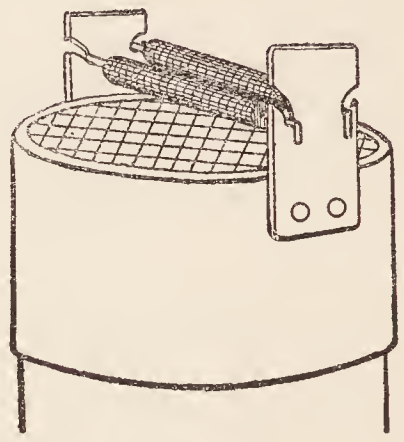


Fig. 28.

size Méker burner is fitted with side pieces, in each of which are slits to receive two fairly stout platinum wires bent at right angles at the ends. Round each wire is rolled a piece of platinum gauze about $1'' + 1\frac{1}{2}''$. Pieces of sodium chloride, which have been fused, are laid on the rolls of gauze after the burner has been lit. The salt melts and sinks into the meshes of the rolls, from which it slowly volatilises. The late Sir W. H. Perkin (Chem. Soc. Trans. 1906, 89, 617) allowed what was practically an oxy-hydrogen flame to play on the side of a platinum boat containing sodium chloride. Another device has been described by H. E. Armstrong (Proc. Roy. Soc. 1908, A, 81, 113). Sodium bromide may be used instead of the chloride, as it gives a more intense light, but a serious disadvantage lies in the fact that the bromine vapour given off may injure the polarimeter.

The light from a burner volatilising sodium chloride is not truly monochromatic. There is a slight continuous spectrum, the blue from the Bunsen flame being fairly strong, so the light is usually filtered through a saturated solution of potassium dichromate, which removes the blue and green rays and is sufficient for most purposes. Sometimes a small cell, 1·5 cm. long containing uranous sulphate solution may be used, in addition to the potassium dichromate, as it removes any red rays that may be present; but the best method of purifying the light is by spectral analysis, a direct vision spectroscope being placed between the eye and the analyser or in front of the polariser. Details of the

former method are given in a paper by Sir W. H. Perkin (Chem. Soc. Trans. 1906, 89, 609).

In a stricter sense, however, sodium light is not monochromatic, for its spectrum consists of two lines very close together, D_1 of $\lambda=589{\cdot}62$ $\mu\mu$ and D_2 of $\lambda=589{\cdot}02$ $\mu\mu$, so that the light reaching the polariser is a resultant whose 'optical centre' lies between these wave lengths in proportion to the relative intensity of the lines, which varies with the density of the vapour in the flame and this might have to be taken account of in very accurate work. It is therefore desirable to keep the brightness of the flame as constant as possible whilst a set of readings is being made. Otherwise as the brightness falls off the readings may vary a little.

Monochromatic light may also be obtained from the mercury arc lamp, in the spectrum of which there are four chief lines, one in the blue of 435·9 $\mu\mu$, two in the yellow of 579 and 576·9 $\mu\mu$ respectively, whilst the strongest and most important is that in the yellow-green of 546·1 $\mu\mu$. The other rays are filtered out by a suitable screen or by some method of spectral purification, and the last line is found very useful for polarimetric purposes (*see* Lowry, Phil. Mag. 1909, [vi.] 18, 320). If this light be utilised, however, comparative measurements with sodium light should always be given, as otherwise much of the value either of the new data or of the data already amassed for sodium light would be lost.

The enclosed cadmium arc may also be used (Lowry and Akram, Trans. Faraday Soc. 1914, 10, 61).

The polarimeter.—Fig. 29 shows diagrammatically a modern polarimeter, as made by Schmidt and Haensch, Berlin, who, however, supply a different heating apparatus. The lamp A is so placed that a sharp image of the flame, or the diaphragm T in front of it, is thrown by the lens S on the diaphragm at M. B is a cell containing saturated potassium dichromate solution. By means of C, the polarising prism D can be

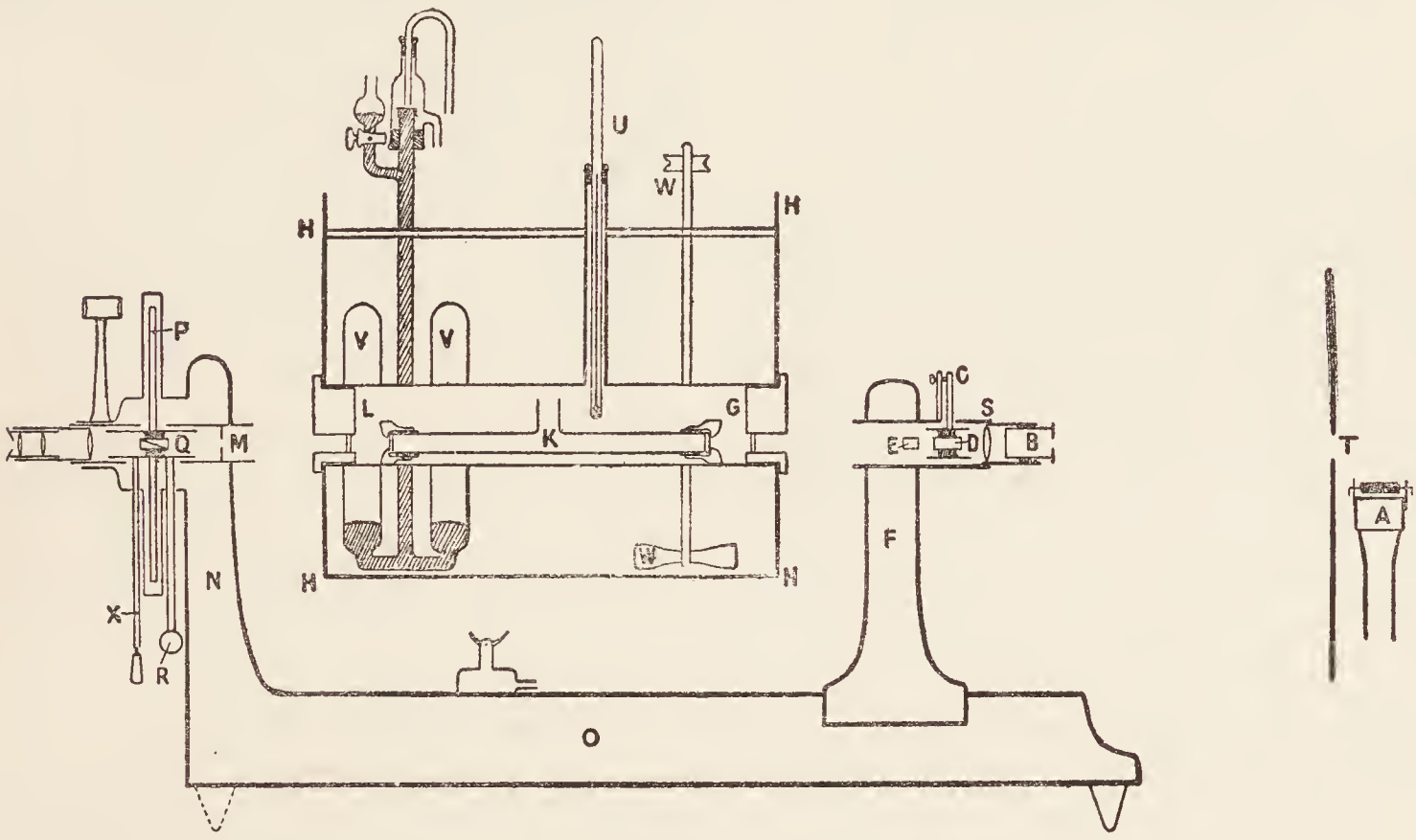


FIG. 29.

turned about its axis of length, and thereby the angle altered which its principal plane makes with the principal planes of the small prisms at E. The heavy support F can be moved along the bed-plate O and clamped in any desired position. The observation tube K lies in a wider tube which passes through a copper bath HHHH containing water or other liquid. This bath is kept at any desired temperature by means of the thermo-regulator V (J. Soc. Chem. Ind. 1902, 21, 456) and the stirrer W. A thermometer U indicates the temperature inside the tube LG, which may be taken as identical with that in the observation tube. LG is closed at L and G by two wooden blocks, the holes in which are closed by small glass discs. Q, the analysing Nicol, is fastened to the graduated circle P, which is enclosed in a cover to protect it from the fumes of the laboratory. The lever X attached to the analyser and the graduated circle, makes the rough adjustment; the fine adjustment is made by means of the screw R. There is also another screw (not shown in the figure) by which the analyser can be turned about its axis independently of the graduated circle to adjust the zero point of the instrument. It may be noticed that when the half shadow —the sensitiveness—is altered by moving the lever C, the zero point is thereby also altered. The sensitiveness ought therefore only to be varied very cautiously and the zero point should be ascertained at frequent intervals, best along with each observation. For an interesting case in point, *see* Chem. Soc. Trans. 1905, 87, 618.

The water in the thermostat HHHH should be covered with a layer of medium paraffin oil, which, by preventing evaporation, tends to keep the temperature constant. By means of the apparatus shown, the bath can be kept within about 0·01° of a given temperature for several months.

For experiments at temperatures above 80°, a rather small bath filled with oil is best—when the temperature can be raised to 170° or still higher if the joints of the bath are brazed.

Another form of heating apparatus is shown

in Fig. 30. P is the polariser and A the analyser of the instrument. Between these, and having the same axis, is supported in some suitable manner, a double cylinder of brass or copper. The observation tube rests in the position shown, and the tubes E and D allow either of a current of water at some definite temperature being circulated through the cylinder or of steam or other vapour such as that of aniline or nitrobenzene being blown through the apparatus until the temperature has become constant in the observation tube. For an illustration of an instrument fitted in just a slightly different

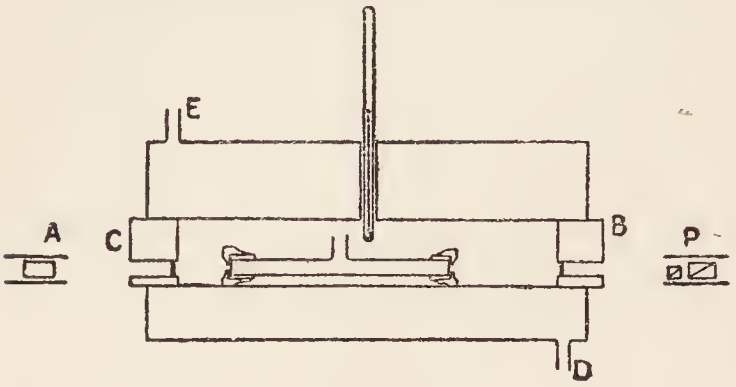


FIG. 30.

manner, *see* Scheuer, Zeitsch. physikal. Chem. 1910, 72, 569.

Polarimeter tubes.—Fig. 31 shows the end of a polarimeter tube of the simplest type. Near each end of the glass tube there is fastened a metal collar having a screw cut on it. The ends of the tube are ground parallel and fitted with discs, A, of glass, which ought always to be carefully examined before use as occasionally they are slightly active on account of internal strain, when they should, of course, be rejected. Metal caps press the glass discs against the ends of the tube, rubber washers equalising the pressure between them. The caps must not be screwed on too tightly as this may cause the discs to become birefringent and vitiate the readings. In some patterns of tube, a bayonet joint is used instead of a screw so that the pressure on the discs is at least always the same.

It has recently been found possible to *fuse*

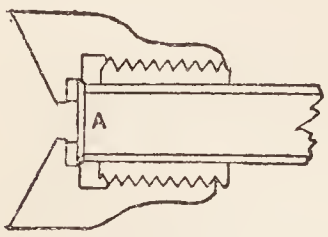


FIG. 31.

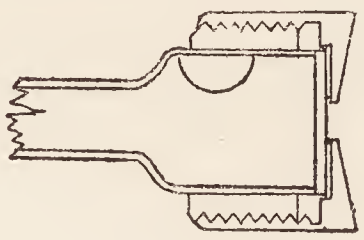


FIG. 32.

the discs to the ends of the tubes, and this should prove to be of great advantage.

In some tubes one end is of the form shown in Fig. 32. Any bubble that has developed owing to contraction on cooling, can easily be moved into the expanded part of the tube where it does not interfere with the field of view. Especially in small tubes, however, the expanded end greatly increases the capacity of the tube, which is often a serious objection, and tubes of the form shown at K in Fig. 29 are much to be preferred, as they readily allow for any contraction or expansion, and can therefore be used for determinations over a moderate range of temperature if care be taken not to melt the sealing wax securing the collars on to which the caps are screwed. Jacketed tubes are also used such that water or other liquid at a desired temperature can be circulated round the tube. This involves the supply of water at constant temperature, which is rather troublesome; a suitable form of apparatus for this is described by Lowry (Trans. Faraday Soc. 1907, 3, 119). With many polarimeters, on account of the form of the stand, this is the only method of heating that can be adopted; but, wherever possible, it is better to use a thermostat like that shown in Fig. 29, which can be adjusted to any required temperature. In sugar factories, for instance, where, especially in the case of invert sugars, it is desirable always to polarise at a definite temperature to avoid the necessity of correcting the readings, a thermostat might be kept at one temperature for, probably, a year at a time without the necessity of renewing any of the parts, and would be found very useful.

Tubes like that shown in Fig. 33, are suitable for investigations over a wide range of temperature. A glass tube with a side piece is fitted, somewhat loosely, at each end with a brass ring K. The discs are then placed in position and short pieces of rubber tubing drawn over the ends of the tube so as to project beyond the discs, thus serving to prevent leakage and as washers as well. Two other brass rings, M, L, are placed, one at each end and secured there by brass rods which pass freely through three holes

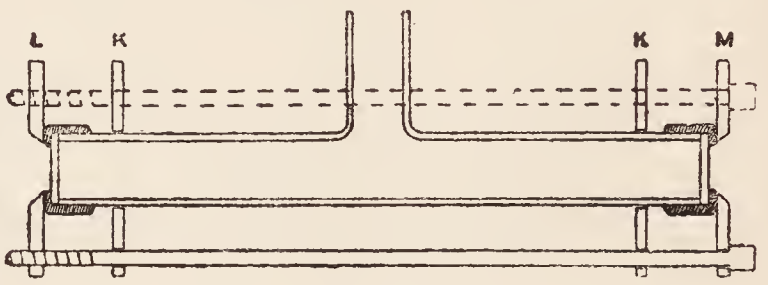


FIG. 33.

in M, K, K, and screw into holes in L. The rings K, K should be near the ends of the tube, their object being to keep it in position between the rings M and L. This tube may be used up to a temperature of about 180°, at which the rubber becomes very soft. For slightly different forms, *see* Chem. Soc. Trans. 1901, 79, 170.

Determination of density.—Another operation of importance in polarimetric work is the determination of the specific gravity of liquids. This may be done by means of a hydrostatic balance, by hydrometers, by the Westphal balance, by specific gravity bottle, by dilatometer or by pyknometer. The last is probably the most accurate as well as the simplest, and is most generally used. For details, *see* article SPECIFIC GRAVITY.

Methods of expressing rotatory power.—Several expressions are in use for indicating the rotatory power of an active compound.

The *observed rotation* is the angle through which the plane of polarisation is turned by a layer of the liquid substance, one decimeter in thickness. Thus $\alpha_D^{20}+34{\cdot}51°$ means that the angle α, through which the yellow light from a sodium flame would be turned to the right—the observer looking *against* the direction of the ray —at 20°, after passing through unit length of

the substance, is 34·51°.[1] If the magnitude of the rotatory power be used merely to indicate the purity of the compound, or for analytical purposes, this expression is as useful as any; but for the comparison of the rotations shown by a given substance under different conditions —of temperature, for instance—it would not be satisfactory, and since Biot's early experiments seemed to show that change of temperature only affected rotation in proportion to the expansion produced, and also that the rotation of a dissolved substance was proportional to its concentration, he introduced the idea of *specific rotation*, which he supposed to be an invariable constant not dependent on the condition of the substance (Mém. de l'Acad. 1835, 13, 116; Ann. Chim. 1844, [iii.] 10, 18). The specific rotation is indicated by the symbol $[\alpha]$, and for a homogeneous liquid $[\alpha]^t_D = \frac{a^t_D}{d}$, where a is the observed rotation for the D line at the temperature $t°$, and d is the density of the substance at $t°$ as compared with water at 4°, as unity.

In the case of a dissolved active compound the strength of the solution must be taken account of, and may be expressed in several ways, the two commonest being as concentration and as percentage composition. Concentration, c, indicates grams of substance per 100 c.c. of solution, the substance being weighed into a graduated flask which is then filled up to some definite volume with the solvent. Then $[\alpha]^t_D = \frac{a^t_D}{c}$. This method, however, is open to the objection that the concentration may, and usually does, vary with change of temperature. In the second case, both active substance and solvent are weighed. The percentage composition, p, is then the weight of substance in 100 grms. of the mixture, and is, of course, independent of the temperature. In this case, $[\alpha]^t_D = \frac{a^t_D}{p \times d}$.

According to Biot, the specific rotation is 'the angle of rotation which a liquid would show if it contained in a volume of one cubic centimetre, one gram of active substance, and should act on the polarised ray through a column one decimetre in length,' but it is simpler to define it as the rotation which would be shown by 10 grms. of the homogeneous substance, or that quantity of solution which contains 10 grms. of it in a tube of 1 sq. cm. cross section, just long enough to contain it. The specific rotation, however, contrary to Biot's early expectations, is by no means necessarily constant, but may vary greatly with temperature, nature of the solvent and concentration.

It is scarcely to be expected that the rotations of different compounds can be compared simply for 10 grms. of each, so the molecular rotation is usually calculated in such cases $[M]^t_D = \frac{[\alpha]^t_D \times M}{100}$. It is the rotation produced by one-tenth of a gram molecular weight of a homogeneous substance, or that quantity of a solution which contains one-tenth of a gram molecular weight, in a tube of one square centimetre cross section just long enough to contain it. This supposes the rotation to be proportional to the whole weight of the molecule, and Guye has suggested that since one looks through the molecule it might perhaps be better to take the rotation as proportional to its diameter, and therefore he introduced the idea of molecular deviation, $[\delta]^t_D = a^t_D \sqrt{\frac{M}{d}}$, but so far it cannot be said that the regularities discovered by the use of this formula are any better than those derived from the molecular rotation, and as it involves greater trouble in calculation it has not been very much used (Compt. rend. 1893, 116, 1454).

[1] Often the rotation observed in any tube is called the 'observed rotation,' the length of tube being specified.

III. Quantitative.

Rotation and chemical constitution.—Although Biot, in his later work, discovered that the rotation of an active compound was a property much more sensitive to external conditions than he had originally imagined, little notice was taken of the fact, and, in consequence, many of the older data, in the collection of which considerations of temperature, solvent, concentration and even the light used, were ignored, are rendered practically useless. Within the last thirty years, however, these factors have received greater attention, and when, for want of a better plan, the rotation values are all taken at one definite temperature, a few regularities appear between the rotation data and the chemical constitution of homogeneous liquid substances.

It is perhaps natural to take first the changes which occur in passing from member to member of a homologous series.

Table I.—Rotation Values of the *l*-Malates.

	$[\alpha]^{20}_D$		$[M]^{20}_D$	
Malic acid [1]	+ 5·89°	12·74°	+7·89°	18·99°
Methyl malate [2]	− 6·85	3·33	−11·10	8·25
Ethyl malate [2]	−10·18	1·44	−19·35	5·97
n-Propyl malate [2]	−11·62	−0·09	−25·32	1·06
n-Butyl malate [3]	−10·72	−0·08	−26·38	0·81
Amyl malate [2]	− 9·92	−3·00	−27·19	−2·42
Capryl malate [2]	− 6·92		−24·77	

Table II.—Rotation Values of the Tartrates.

		$[\alpha]^{20}_D$		$[M]^{20}_D$
Tartaric acid [4]	.	−0·30°	2·37°	−0·45°
Methyl tartrate [5]	.	+2·07	5·67	+3·68
Ethyl tartrate [5]	.	+7·74	4·94	+15·95
n-Propyl tartrate [5]	.	+12·68	−2·38	+29·66
n-Butyl tartrate [6]	[19°]	+10·30		+26·99

[1] Extrapolated from data by Schneider (Annalen, 1881, 217, 257) from aqueous solutions.
[2] Walden, Zeitsch. physikal. Chem. 1895, 17, 245.
[3] Anschutz and Reiter, *ibid.* 1895, 16, 419.
[4] From data by Thomsen, J. pr. Chem. 1885, [ii.] 32, 213.
[5] Pattersen, Chem. Soc. Trans. 1904, 85, 765.
[6] Freundler, Bull Soc. chim. 1894, [iii.] 11, 305.

TABLE III.—ROTATION OF VARIOUS ESTERS DERIVED FROM GLYCERIC ACID.[1]

	A Glycerate $[M]_D^{15}$	B Diacetyl-glycerate $[M]_D^{15}$	A–B	C Dimethoxy-propionate $[M]_D^{15}$	A–C
Methyl	−5·76°	−24·56°	18·8°	−103·8°	98°
Ethyl	−12·30	−35·56	23·26	−114·4	102·1
n-Propyl	−19·15	−45·17	26·06	−122·5	103·3
sec-Propyl	−17·49	41·69	24·20	—	—
n-Butyl	−21·37	—	—	−124·2	102·8
*iso*Butyl	−23·05	−50·38	27·33	—	—
n-Heptyl	−23·05	−47·89	24·84	−127·9	104·8
n-Octyl	−22·28	−47·92	25·64	−125·6	103·3

TABLE IV.

		$[M]_D^{20}$
Menthyl	formate	−146·3°
,,	acetate	157·3
,,	propionate	160·2
,,	*n*-butyrate	157·1
,,	*n*-valerate	157·3
,,	*n*-caproate	157·7
,,	*n*-heptylate	157·7
,,	*n*-caprylate	155·8

TABLE V.—SECONDARY ALCOHOLS.

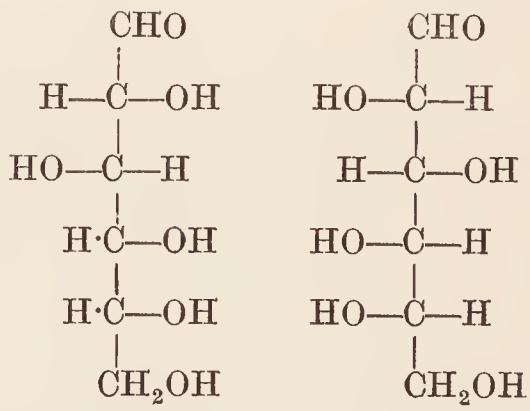
		$[M]_D^{20}$
sec-Propyl-methyl-carbinol		+4·3°
,,	ethyl ,,	15·4
,,	*n*-propyl ,,	24·7
,,	*n*-butyl ,,	33·3
,,	*n*-amyl ,,	32·9
,,	*n*-hexyl ,,	33·9
,,	*n*-octyl ,,	34·5
,,	*n*-decyl ,,	34·5

(Pickard and Kenyon, Chem. Soc. Trans. 1912, 101, 624).

With the above data several points may be illustrated.

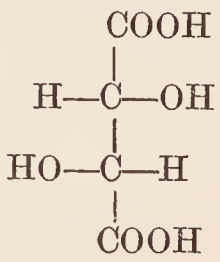
1. Whereas ordinary malic acid in moderately dilute aqueous solution is lævo-rotatory like the esters derived from it, and is called *l*-malic acid, it is to be inferred from the behaviour of its concentrated solutions that the substance, if it could exist at the ordinary temperature in the liquid form, would show a positive rotation. Solutions more concentrated than $p=34$ have a positive rotation at 20°. Tartaric acid, Table II., behaves similarly, but in an opposite sense, for although it itself and its salts in aqueous solution as well as its simple esters in the homogeneous state, have a positive rotation and it is called *d*-tartaric acid, it would nevertheless give, if it could exist in the liquid homogeneous condition, a negative rotation.

2. Although to the names of many compounds the letters *d*- and *l*- are prefixed merely to indicate the sign of their rotation, Emil Fischer has been able to trace a genetic relationship between many substances related to the sugars, and prefixes the letters *d*- and *l*- to the names of compounds according to the structural relationship which they bear to glucose. In a long series of researches, pre-eminent alike for manipulative skill and reasoning power, Fischer has shown that natural glucose must have one or other of the structural formulæ:



d-Glucose. *l*-Glucose.

and as it is hardly probable that we shall ever be able finally to discriminate between these, he has made the above arbitrary selection. *d*-Tartaric acid must then be, as he has shown,



d-Tartaric acid

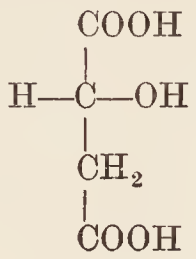
TABLE VI.—ROTATION OF ESTERS OF VARIOUS ACIDS[2] (temperature approximately 20°).

Ethyl	$[M]_D$	Ethyl	$[M]_D$	Ethyl	$[M]_D$	Ethyl	$[M]$
Lactate	−12·2°	Glycerate	−12·3°	Malate	−19·8°	Tartrate	+15·86°
Acetyl-lactate	−79·7	Diacetyl-glycerate	−35·6	Acetyl-malate	−52·3	Diacetyl-tartrate	+10·0
Benzoyl-lactate	+59·0†	Dibenzoyl-glycerate	+89·2	Benzoyl-malate	−11·4	Dibenzoyl-tartrate	−123·6
Methoxy-propionate	−118·9	Dimethoxy-propionate	−114·4	—	—	—	—
Methyl		**Methyl**		**Methyl**		**Methyl**	
Lactate	−8·6	Glycerate	−5·8	Malate	−11·1	Tartrate	+3·8
Methoxy-propionate	−112·7	Dimethoxy-propionate	−103·8	Methoxy-succinate	−92·4	Dimethoxy succinate	+180·0†

[1] For references, *see* P. F. Frankland and Gebhard, Chem. Soc. Trans. 1905, 87, 865.

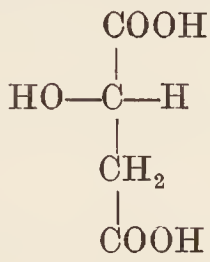
[2] From P. F. Frankland and Gebhard, Chem. Soc. Trans. 1905, 87, 867, which see regarding data marked thus †.

the two upper asymmetric carbon atoms of the glucose molecule corresponding to the two asymmetric atoms of tartaric acid. For *d*-malic acid the formula is



d-Malic acid.

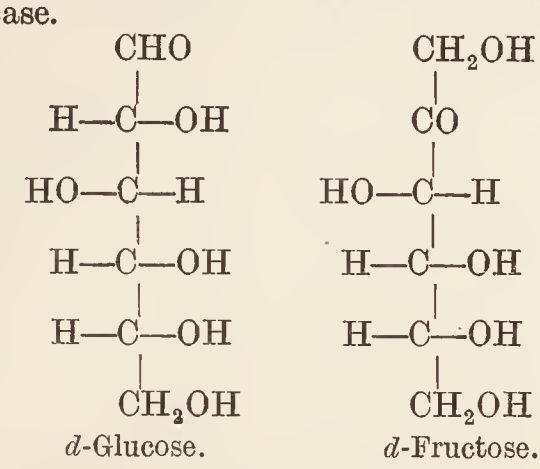
and the structure of its isomeride, ordinary natural *l*-malic acid, will be represented by



l-Malic acid.

(Ber. 1896, 29, 1377).

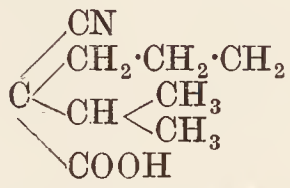
Thus, although for ethyl dibenzoyltartrate $[M]_D^{20} = -123{\cdot}6°$ (Table VI.), the substance is nevertheless a *d*-compound. Similarly, fructose with a high negative rotation is *d*-fructose on account of its structural relationship with *d*-glucose, the configuration about the three lowest asymmetric carbon atoms being the same in each case.



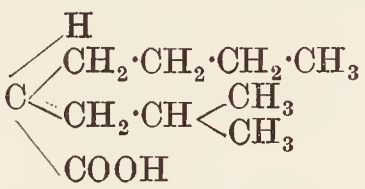
d-Glucose. *d*-Fructose.

3. Table I. shows that the specific rotation of the malates becomes increasingly more negative as the series is ascended until the *n*-butyl ester is reached, and from this point the rotation rises again. There is thus a minimum (maximum negative) rotation at the *n*-propyl term. When the molecular rotation is considered, however, the behaviour is not the same, the lowest rotation occurring at the amyl term. With the tartrates, on the other hand, a maximum occurs both in the molecular, and the specific, rotation, at the same—the *n*-propyl —term. In the molecular deviation for these different esters the minimum might possibly be found at some other term. The example illustrates a kind of difficulty that often occurs; we have no criterion to decide which method of reducing the observations is the best, but the molecular rotation is probably to be preferred to the specific rotation.

This tendency to rise to a maximum and then fall again may be seen in all the data of Table III., and has been much discussed in connection with an idea put forward almost simultaneously by Crum Brown (Proc. Roy. Soc. Edin. 1890, 17, 181) and by P. A. Guye (Compt. rend. 1890, 110, 714; 1893, 116, 1378, 1415), who suggested that a relationship might be detected between the rotation of a compound and the masses of the four radicles attached to the asymmetric atom. Guye proposed, for calculating the 'Product of Asymmetry,' a formula of such a character that when two of the masses became equal the expression reduced to zero. The formula predicted also the occurrence of maximum rotations at definite members of certain series, and in some cases maxima were found at, or about, these terms. But for the most part it failed entirely; the rotation of a compound does not become zero merely because two of the groups attached to the asymmetric atom are equal in weight. Fischer and Flatau (Ber. 1909, 42, 2981) have shown that, for instance, the isomerism between *n*-propyl and *sec*-propyl is sufficient to render them different groups so far as an asymmetric carbon atom is concerned. Thus *n*-propyl-*sec*-propyl—cyanoacetic acid



was found to have a rotation $[\alpha]_D^{20} = +11{\cdot}3°$ in toluene solution $p = 10{\cdot}4$, and *n*-butyl-*iso*-butyl-acetic acid



had in the homogeneous state $[\alpha]_D^{22} = +5{\cdot}73°$ (Fischer, Holtzapfel and v. Gwinner, Ber. 1912, 45, 247), and *n*-propyl-*sec*-propyl carbinol has $[M]_D^{20} = +24{\cdot}7°$ (Pickard and Kenyon, Chem. Soc. Trans. 1912, 101, 624, Table V.).

4. Tables I., III. and V. show that the molecular rotation alters most rapidly in passing through the lower members of a homologous series, a comparative constancy being reached in the higher representatives. These are examples of a regularity first pointed out by P. F. Frankland and MacGregor (Chem. Soc. Trans. 1896, 69, 121), namely, that when substitution takes place in a molecule at a point comparatively remote from the asymmetric atom it is attended with but little change in rotatory power. Tschugaeff gives the data of Table IV. to show that: 'In every series of homologous derivatives of any asymmetric substance there occurs, at least within certain limits, an inverse proportionality between the values of the specific rotation and the corresponding molecular weight' (Ber. 1898, 31, 366). To these may be added the data by Pickard and Kenyon in Table V. According to Frankland, the general behaviour, especially the existence of a somewhat indistinct and irregular maximum, may be explained thus: 'According to the commonly accepted views of stereochemistry, a continuous chain of five carbon atoms will all but return upon itself, and, beyond this, further additions to the chain will lead to such interference as must necessitate a readjustment of the exact positions occupied

by the carbon atoms in a shorter chain. It is surely highly probable that this stereochemical change should be betrayed by some irregularity in the rotatory manifestations, for example, by the exhibition of a maximum rotation in those series in which the ascent of the series leads to an increase in the rotatory power' (Chem. Soc. Trans. 1899, 75, 368; 1912, 101, 658).

5. A regularity emerging from the data of Table VII. was first pointed out by McCrae and Patterson (Chem. Soc. Trans. 1900, 77, 1108).

TABLE VII.—ROTATION OF SUBSTITUTED ETHYL TARTRATES.

(Ethyl tartrate, $[M]_D^{20} = +15{\cdot}86°$.)

Substituent	$[M]_D^{20}$	Substituent	$[M]_D^{20}$
Mono-acetyl .	+23·1°	Di-acetyl .	+9·9°
,, monochloracetyl .	32·3	,, monochloracetyl .	+25·5
,, trichloracetyl .	54·7	,, trichloracetyl .	+67·1[1]
,, phenacetyl	98·5	,, phenacetyl .	+79·2
,, benzoyl .	61·4	,, benzoyl .	−247·1
,, *o*-toluyl .	38·2	,, *o*-toluyl .	−266·5
,, *m*-toluyl .	44·0	,, *m*-toluyl .	−306·3
,, *p*-toluyl .	63·5	,, *p*-toluyl .	−484·4
,, nitro .	89·23[2]	,, nitro .	+80·45[2]
,, *m*-nitrobenzoyl	44·38[3]	,, *m*-nitrobenzoyl .	−357·3[4]

One acyl group, introduced into the molecule of ethyl tartrate, brings about in each case a considerable increase of rotation, whilst the introduction of a second (with the one exception of the trichloracetyl derivatives) causes a diminution, which for the purely aromatic radicles, benzoyl and the toluyls, is very great indeed, the positive rotation of the monosubstitution product being changed into a very high negative rotation.

6. Another question that has attracted attention relates to the effect upon rotation of the presence of multiple bonds. It is often asserted that a double bond raises the rotation, but as the following figures show this general statement requires qualification.

TABLE VIII.

Menthyl ester of (Alcoholic solution $p=9$)	$[M]_D^{20}$
Butyric acid . .	−164·7°
Crotonic ,, . .	203·1
$\Delta^{\alpha\beta}$-Pentenonic acid . .	177·1
$\Delta^{\beta\gamma}$,, ,, . .	172·5
$\Delta^{\gamma\delta}$,, ,, . .	160·2
$\Delta^{\alpha\beta}$-Hexenoic ,, . .	172·4
$\Delta^{\beta\gamma}$,, ,, . .	164·1
$\Delta^{\gamma\delta}$,, ,, . .	153·5
$\Delta^{\delta\epsilon}$,, ,, . .	154·4
$\Delta^{\alpha\beta}$-Heptenoic ,, . .	175·5

(Rupe, Annalen, 1903, 327, 166).

The double bond exerts a greater effect the nearer it is to the asymmetric centre. Menthyl butyrate has, almost exactly, what Tschugaeff calls the constant molecular rotation for the menthyl esters, but when a double bond is introduced into the molecule to give menthyl crotonate, the rotation is very markedly augmented, the same thing on a smaller scale being noticeable for the other unsaturated acids in which the double bond is in the $\alpha\beta$-position. As the double bond moves further from the asymmetric centre the rotation gradually reverts to the normal value, the behaviour being thus in accordance with the regularity of Frankland and MacGregor already alluded to under 4.

Rupe has also shown that the rotation of menthyl sorbate

$$CH_3—CH=CH—CH=CH—\overset{\overset{O}{\|}}{C}\cdot O\cdot C_{10}H_{19}$$

$[\alpha]_D = -88{\cdot}53°$, is much higher than that of $\Delta^{\beta\gamma}$-hexenoic acid menthyl ester

$$CH_3—CH_2—CH=CH—CH_2—CO\cdot O\cdot C_{10}H_{19}$$

$[\alpha]_D = -65{\cdot}11°$, which he attributes to the presence of a system of alternate single and double bonds, such as has been called by Thiele, conjugated, the menthyl sorbate containing a set of three conjugated double bonds.

No perfectly general rule regarding the influence of double bonds can be formulated, however; thus it has been shown by Frankland and O'Sullivan (Chem. Soc. Trans. 1911, 99, 2327) that, whereas the rotation of propyl menthoxyacetate is less than that of allyl menthoxyacetate at 20°, it is greater at a temperature of 100°, whilst at about 38° the rotations of the two substances are equal. The effect of multiple bonds has been examined in a number of cases by Hilditch (*ibid.* 1909, 95, 1581).

In regard to the relative influences upon rotatory power which a substituent exerts in the *ortho*, *meta*, and *para* positions respectively, it has generally been found that the *para* disubstitution product has the greatest rotation and the *ortho* the least, whilst the phenyl derivative usually comes in between the *ortho* and the *meta* compounds (P. F. Frankland, Chem. Soc. Trans. 1896, 69, 1538; 1912, 101, 666; Cohen and Dudley, *ibid.* 1910, 97, 1737).

These observations represent only a very crude and tentative attempt at a generalisation of the subject, as must be obvious when it is borne in mind that the rotation of an active compound is dependent not only on its constitution, but apparently to quite as great an extent on various external circumstances—on the temperature, the colour of light used, the nature of the solvent in which the compound may be dissolved; whilst, in the last case, the temperature and the colour of the light have to be considered afresh, since their effects upon the rotation of a solution of an active substance may be entirely different from their effects upon the rotation of the substance itself. It may therefore be said that the rotation of an active compound varies with at least six other factors.

In recent years some fairly comprehensive work involving most of these factors has been carried out, and it has been shown possible to discuss the whole subject from a single point of view. This point of view is best arrived at by considering in the first place the effect of temperature-change upon rotation, and thereafter the influence of solvents and the colour of light used.

[1] Patterson and Davidson, Chem. Soc. Trans. 1912, 101, 387.

[2] In 9 per cent. methyl alcoholic solution, Frankland, Heathcote and Hartle, *ibid.* 1903, 83, 154.

[3] In 2·38 ethyl alcoholic solution, Frankland, Heathcote and Green, *ibid.* 1903, 83, 168.

[4] Homogeneous; Frankland and Harger, *ibid.* 1904, 85, 1578.

Influence of change of temperature on rotation.—The early experiments of Biot indicated that temperature played a quite unimportant part in conditioning the rotation of active bodies, but later investigations, chiefly by P. F. Frankland, have shown that, in reality, its influence is of the greatest consequence. Rotation may increase or diminish with change of temperature, or it may appear to remain almost unaffected, but it is probable that when examined over a sufficient range, the rotation of an active compound will show a maximum or a minimum value, or perhaps several such. An idea of the behaviour met with will be obtained from Fig. 34, which represents the influence of temperature change upon the molecular rotation of a number of closely related substances.

Methyl tartrate (not represented in the figure) is practically inactive at 0°, and if cooled below this temperature its rotation becomes negative ;

Temperature Rotation Curves for Various Esters of Tartaric Acid.

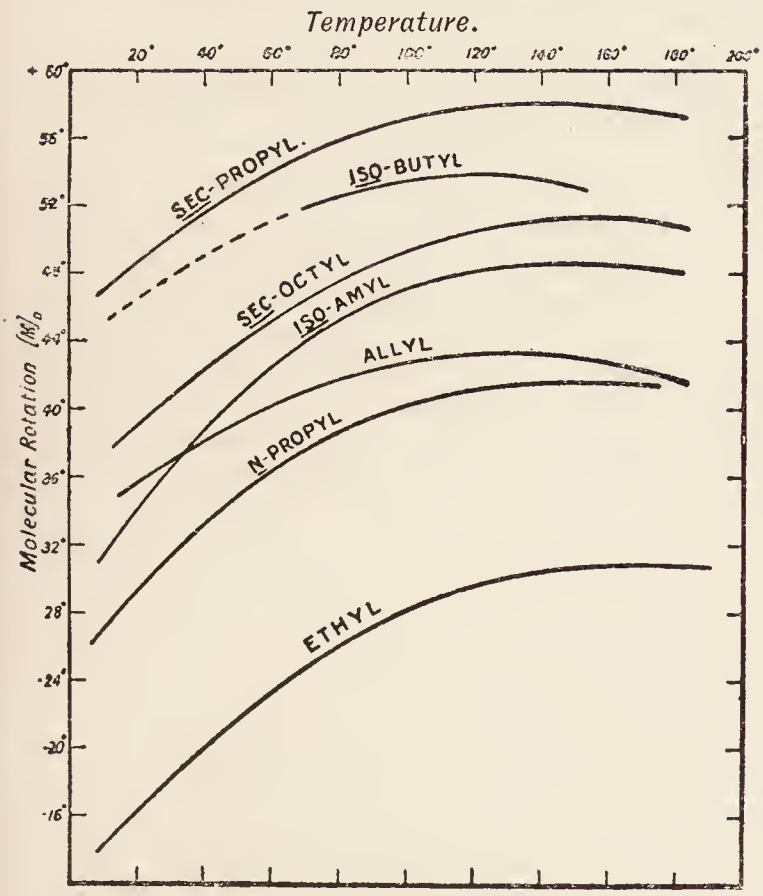


FIG. 34.

it therefore furnishes an example of a compound whose rotation passes through the point of inactivity at some definite temperature for light of a particular wave length. The rotation of ethyl tartrate is higher than that of the methyl ester and the increase of rotation on heating is somewhat greater. The point of inactivity would be reached about −34°. All the curves shown are, in general, alike, but even for such closely similar substances, the institution of comparisons between the rotation values at any one given temperature cannot yield very satisfactory results. The rotation values for these esters at 20° would not be in the same sequence as at, say, 180°. At the former temperature, allyl tartrate, for instance, has a higher rotation than has *iso*-amyl tartrate, whereas at the latter the reverse is the case. Other examples are obvious.

The most important things to notice about these curves are, firstly, their general resemblance, and secondly, the existence in each of a maximum, a singular point which can easily be recognised, and which, presumably, represents some analogous internal condition of each substance. The position of this maximum in the various curves tends to move slightly towards the left of the diagram—to occur at a lower temperature the higher the rotation of the ester. Thus it is clear that in the neighbourhood of 140° ethyl tartrate and *iso*-butyl tartrate, two analogous esters, display an exactly opposite behaviour—the rotation of one increasing with rise of temperature and that of the other diminishing. Such an opposite behaviour is, in fact, frequently found, in much more exaggerated fashion, for closely similar substances ; for example, the rotation of an aqueous solution of sodium tartrate ($p=1{\cdot}499$) increases with rise of temperature, whereas that of a similar solution of ethyl tartrate diminishes (Chem. Soc. Trans. 1904, 85, 1117, 1129). It therefore seems quite probable that when such conflicting behaviour is met with it may be assumed that whilst both compounds have a similar type of temperature-rotation curve, one of them is represented by the ascending branch and the other by the descending branch, in the circumstances of the experiments.

Attempts are often made to express mathematically the relationship between rotation and temperature, the parabolic equation

$$a=a+bt+ct^2$$

being usually applied. Such a curve does show a maximum value, but since the parabola is symmetrical the two limbs of a T-R curve accurately represented by this formula would necessarily be of the same shape, and therefore the rotation ought to increase or diminish constantly to infinity on either side of the maximum. Winther (Zeitsch. physikal. Chem. 1902, 41, 176) has calculated such an equation for ethyl tartrate and reduced it to the form

$$[\alpha]^t_D=14{\cdot}126-0{\cdot}000401[t-149]^2$$

the temperature 149° being that of the maximum rotation. He suggested that the value of the specific rotation should be reckoned, not from zero, but from this maximum value, such a datum to be called the 'rational specific rotation,' $[A]^t_D$.

$$[A]^t_D=a-[\alpha]^{t^\circ}_D=b[t-149]^2$$

(*l.c.* 207).

Winther assumes that the temperature at which the maximum occurs is the same at least for the three esters with which he deals, but this is not the case (Patterson, Chem. Soc. Trans. 1908, 93, 1844). The curves of Fig. 34 show maximum rotations at temperatures as below.

TABLE IX.

Ester	Temperature	Maximum $[M]_D$
Ethyl tartrate	175°	+30·9°
n-Propyl ,,	150	41·65
sec-Propyl ,,	144	58·03
iso-Butyl ,,	120	53·9
iso-Amyl ,,	151	48·72
Allyl ,,	130	43·24
sec-Octyl ,,	160	51·46

It may be, however, that the maximum rotations occur at 'corresponding' temperatures at which it would be legitimate to compare with one another the rotation values of different active compounds, or that comparison should be made at temperatures connected in some simple manner with those at which the maxima occur. A suggestion of this sort was made by Patterson (Chem. Soc. Trans. 1904, 85, 765), based on the fact that the rotations of methyl, ethyl, and *n*-propyl tartrate would respectively become zero at 0°, −34°, and −60°; these may be 'corresponding' temperatures, and, as a first approximation, the rotations, of methyl tartrate, of ethyl tartrate, and of *n*-propyl tartrate may be directly comparable at T°, (T −34°), and (T −60°) respectively. The ratio of the rotations of the esters thus obtained remained nearly constant over a fairly wide range of temperature.

Although it is of considerable interest to investigate the shape of the T-R curves, the

Temperature Rotation Curves for Various Esters.

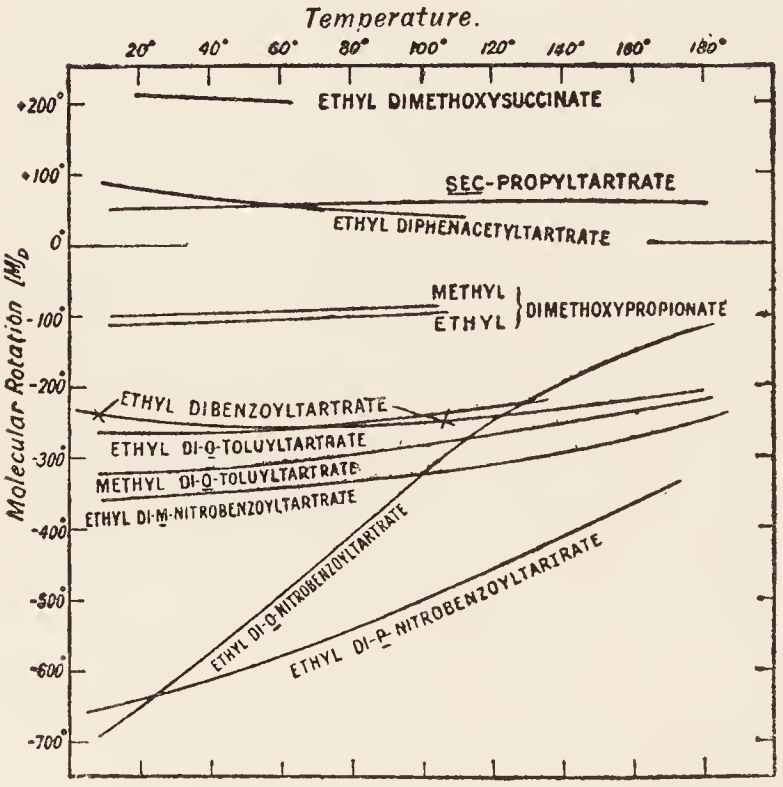


FIG. 35.

direct examination of the rotation of an active compound over a sufficiently wide range of temperature is, unfortunately, for various reasons, a difficult matter, and, meanwhile, it is only possible to proceed by piecing together such evidence from different sources, as bears on the question. Some of this is shown in Fig. 35, in which the scale of the rotations is very much smaller than in Fig. 34, the graph for *sec*-propyl tartrate being included for comparison.

The uppermost curve represents the behaviour of ethyl dimethoxysuccinate, the rotation of which, $[M]_D^{20} = +210{\cdot}6°$, falls to 199·8° on heating to 60°. With this may be compared the curves for the methyl and ethyl esters of dimethoxypropionic acid, which have rotations at 20° of about −100°, becoming less negative as the temperature rises. These dimethoxypropionates are derived from *l*-glyceric acid which, in its configuration, corresponds to *l*-tartaric acid, so that the dimethoxypropionates, corresponding to *d*-tartaric acid, would have positive rotations of about +100°, gradually falling with rise of temperature, and would thus show a behaviour closely analogous to that of the dimethoxysuccinates, which with two asymmetric centres have a rotation almost twice as great. The other curves on the diagram represent data obtained by P. F. Frankland and his pupils, and exhibit the very great effect which change of temperature may exert. That for ethyl dibenzoyltartrate is of especial interest as it shows a minimum of −258° at a temperature of 63° (Frankland and Wharton, Chem. Soc. Trans. 1896, 69, 1587). It was the first recorded instance of this phenomenon, but a considerable number of other cases have since been found. All the curves in Fig. 34 show distinct maxima, and maxima also exist in the temperature-rotation curves for ammonium and sodium molybdanylbimalates (Grossmann and Pötter, Ber. 1904, 37, 84), for solutions of sodium and potassium tartrates, for some of the potassium alkyl tartrates (Patterson, Chem. Soc. Trans. 1904, 85, 1116) and for homogeneous menthol (Patterson and Taylor, *ibid.* 1905, 87, 33) and in other cases.

The remaining curves represent the results of observations by Frankland and Wharton (Chem. Soc. Trans. 1896, 69, 1309, 1583) and Frankland and Harger (*ibid.* 1904, 85, 1571). That for ethyl dibenzoyltartrate is much like the graph for ethyl di-*o*-toluyltartrate, whilst those for ethyl di-*m*-nitrobenzoyltartrate and ethyl di-*p*-nitrodibenzoyltartrate are again very much alike. The behaviour of ethyl di-*o*-nitrobenzoyltartrate is most remarkable. The very high negative rotation diminishes with surprising rapidity as the temperature rises, and appears to have a point of inflection somewhere between 80° and 100°. The degree in which relationship between rotation and constitution depends on the temperature of comparison is strikingly apparent from this set of substances. At a low temperature, the *o*-nitrobenzoyl derivative has the greatest negative rotation, whilst at a temperature of 135° it would have the lowest, its graph cutting the other curves at intermediate temperatures. Nevertheless it is probably of the same type as the others. The rotation of ethyl dibenzoyltartrate is a minimum at 63°, and it seems likely that the di-*o*-toluyl derivative will reach a minimum value at a somewhat lower temperature, and similarly for the *m*-nitrobenzoyl derivative. The slope of the curve for ethyl di-*p*-nitrobenzoyltartrate is greater, and therefore its minimum should lie at a still lower temperature. In an analogous manner the last curve may also have a minimum of high numerical value at an even lower temperature. On the other hand, the di-*o*-nitrobenzoyl derivative may rise to a maximum, and it is probable that ethyl di-*p*-nitrobenzoyltartrate and the other esters also have maxima at successively higher temperatures. If this be true, the variation of the rotation of an active compound with change of temperature is a *periodic* phenomenon, and several maxima and minima might be expected to occur as one or other of the groups attached to the asymmetric atom preponderates. Unfortunately it is difficult to examine the variation over a wide range of temperature.

The effect of temperature-change upon the

rotation of the di-trichloracetyl derivatives of ethyl and *iso*butyl tartrate is of interest in connection with this idea (Chem. Soc. Trans. 1913, 103, 152). In both cases a minimum is apparent in the graphs, that for the ethyl ester occurring at the lower temperature. In appearance the curves are thus just the opposite of those to which they might reasonably be expected to be closely similar—those for ethyl and *iso*butyl tartrates. Therefore it would seem that just as the introduction of two benzoyl, or substituted benzoyl, groups in ethyl tartrate apparently brings into view a minimum in the T-R graph of the resulting compound, which in pure ethyl tartrate would only be found at quite low temperatures, so the introduction of the trichloracetyl groups shifts the general T-R curve in such a manner as also to bring into view a minimum, which, however, from the moderately large value of the rotation, is more likely to be one occurring at a high temperature in the homogeneous parent esters. Thus if one of the tartrates could be examined over a much wider range of temperature than is at present possible, it seems reasonable to suppose that the T-R graph obtained would, in a qualitative sense, resemble any one of the three curves shown in Fig. 41. There would be a minimum (of small negative value) at a low temperature; the curve would then rapidly rise to reach a maximum (of moderate positive value); and then fall again to reach another minimum (also of positive value). It would appear that change of constitution in passing from one derivative to another, or the action of a solvent, has the effect of shifting the position, and altering the shape, of a general type of curve.

Optical Activity of Vapours.

It may be added that when turpentine was converted into vapour it still retained its optical power (Biot, Ann. Chim. 1819, [ii.] 10, 73) and the same thing has been observed for certain derivatives of amyl alcohol (Guye and do Amaral, Arch. sc. phys. Genêve, 1895, [iii.] 33, 409, 513; Compt. rend. 1895, 120, 1345; Wied. Beibl. 1895, 19, 792, 894).

Influence of Temperature-Change upon Rotation in Solution.

In solution the rotation of an active substance is, in general, different, and often greatly different, from what it is in the homogeneous condition. Thus, for example, from the curves in Fig. 37, it will be seen that the addition of 25 p.c. of water to ethyl tartrate has the effect of raising the specific rotation at 20°, from +7·7° to nearly +11°. In a similar manner the addition of 91 p.c. of acetylene tetrachloride lowers the specific rotation at 20° to −16°. The general effects produced by change of concentration will be dealt with in the next section, but since the cause of the influence of solvents is clearest when the effect of temperature-change upon rotation in solution is considered, this aspect of the question will first be dealt with.

Influence of Temperature Change on Rotation in Solution.

Alteration of the temperature of a solution is generally accompanied, as in the case of a homogeneous compound, by a corresponding alteration in rotation. The case of ethyl tartrate has been examined fairly completely and the curves of Fig. 37 will help to explain the results obtained; the thick graph represents the change of rotation of the undiluted ester.

In a solvent such as acetylene tetrachloride, $p=9{\cdot}3$, which, at 20°, has a powerful depressing effect, the rotation rises rapidly with increase of temperature, whilst in a solvent like α-nitronaphthalene, $p=5$, which greatly raises the rotation of the ester, rise of temperature diminishes the rotation with almost equal rapidity. Other solvents, or the same solvents at intermediate concentrations, produce effects lying

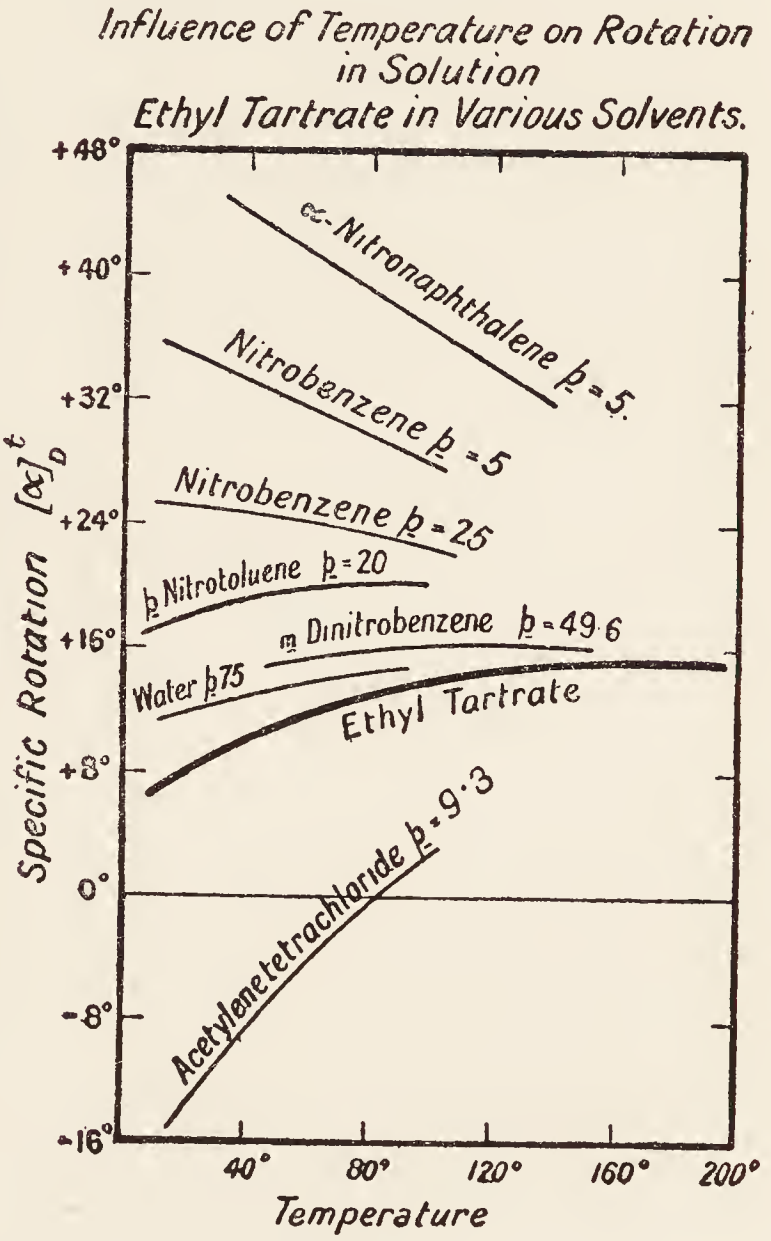


FIG. 36.

between these extremes, in such a manner that, roughly speaking, the whole series of curves gives the impression of a gradual variation of some property irrespective of the chemical composition of the solvents. It is interesting that, whilst the maximum rotation of the homogeneous ester lies at a temperature of 175°, it is again quite apparent in a solution in *m*-dinitro-benzene of $p=49{\cdot}6$, but at a lower temperature, 123°. The curve for *p*-nitrotoluene, $p=20$, shows a maximum at about 85°, and, from the appearance of the other curves, the maximum passes rapidly to lower temperatures as the rotation increases.

Now it was remarked, p. 353, that the maximum in the T-R curves for the tartrates occurred at slightly different temperatures in

passing from one ester to another. There is a slight shift in this singular point in accordance with the slight change in constitution, and it was suggested that in passing to the di-trichloracetyl derivatives a greater shift of the whole T-R curve takes place, so as to bring an entirely different part of a general curve into view.

From the above diagram and also from much other evidence of a similar character it appears that the effect of a solvent upon the rotation of an active compound is of just the same kind. The point of maximum rotation is shifted to the right or left of the diagram and raised or lowered according as the solvent raises or depresses the rotation of the compound, or in the case of a solvent with little effect the course of the T-R curve is practically unaltered. Thus the graph for ethyl tartrate in acetylene tetrabromide, Fig. 37, corresponds to the region *bcde* of the general T-R curve, Fig. 41, whereas that for the nitrobenzene solution of $p=5$, corresponds to the region *hi*. If this be the case it is to be supposed that curves such as those for ethyl tartrate in nitrobenzene, $p=5$, and in α-nitronaphthalene, $p=5$, are tending towards minima which would correspond to that in the region *klm* in the general curve of Fig. 41. In these two solvents no minimum is observable, but the graph for ethyl tartrate dissolved in quinoline, $p=10$, does actually exhibit a minimum at a temperature of 94° and a specific rotation of $[M]_D=+16{\cdot}5°$ (Chem. Soc. Trans. 1913, 103, 161). It will be shown further on in connection with rotation-dispersion that this minimum is, with very great probability, that which would occur in the homogeneous ester at a high temperature.

Rotation in solution. Concentration effect.—In the last section the influence of solvents upon rotation was dealt with from the point of view of T-R graphs. It is commoner, perhaps, to study the variation of rotation with change of concentration at some fixed temperature. The phenomena then met with may be illustrated by the behaviour of ethyl tartrate in water.

The rotation of the homogeneous ester, at 20° ($l=1$ decimetre), is 9·4°, and if the tube were extended to twice its original length, without alteration of the cross section, water being added to fill up the resulting space, the rotation of the 2 decimeter layer of solution, after thorough mixing, would be 20·4°, or more than twice as much as before. If the tube were again doubled in length and more water added, the rotation would become 27·6°, and on continuing the process until the tube could be considered infinitely long, a rotation of 32·3° would ultimately be reached.

The curves shown in Fig. 37 represent the effect of several solvents of very different character, not upon the observed, but upon the specific rotation of this ester, at 20°. For pure homogeneous ethyl tartrate $[\alpha]_D^{20}=+7{\cdot}8°$, and this increases on mixture with water in such a manner as to reach the value +26·84° in an extremely dilute solution. In nitrobenzene, the increase of rotation is much the same as in water but the curve is different in shape and the effect of the solvent is greater, the rotation in very dilute solution being raised to +41°. In ethyl alcohol, the rotation diminishes slightly to reach a minimum value at a concentration of $p=60$, after which it increases to a final value of +9·13°. The behaviour of benzaldoxime is very remarkable: the rotation of the ester increases until $p=70$, at which point a maximum value of +13·6° is reached. Further addition of oxime then diminishes the rotation, so that at $p=22$ the solution becomes inactive, and at infinite dilution the specific rotation would be approximately −16°. The rotation therefore varies 30° between the extreme limits, and by about equal amounts on either side of zero (Chem. Soc. Trans. 1907, 91, 508). In acetylene tetrabromide the rotation of the dissolved ethyl tartrate diminishes very rapidly with diminution of concentration, the

Influence of Various Solvents on the Rotation of Ethyl Tartrate.

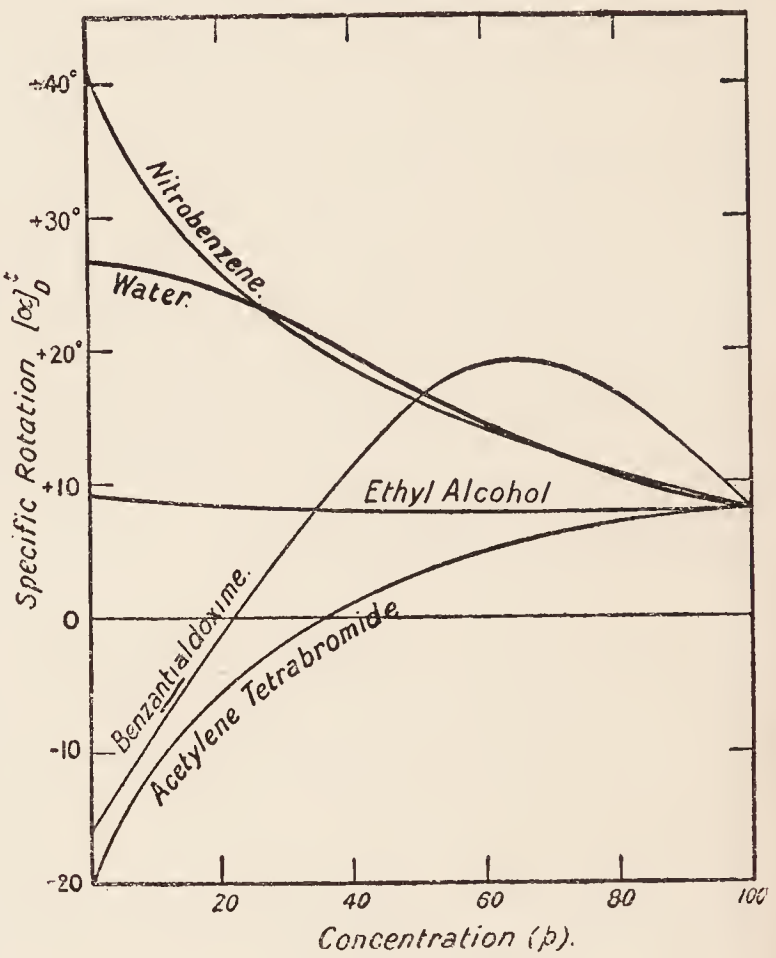


FIG. 37.

rate becoming greater as the dilution increases, to attain ultimately to a value of −20°.

Thus the rotation of this ester, whose specific rotation in the pure condition is only +7·8°, can be made to vary from +41° to −20° by solution in these solvents; clearly, therefore, care must be taken in reporting the exact circumstances under which any rotation has been measured, and also in utilising rotation data obtained by the use of several different solvents. The curves also show that if an active compound is solid, so that its rotation in the homogeneous liquid condition cannot be determined, this value may still be arrived at by extrapolation from the data for its solutions, preferably in a number of solvents, the accuracy with which the extrapolation could be made depending, of course, on the solubility of the compound.

Many attempts have been made to explain

these remarkable effects. Naturally a correlation has been suggested between the rotation and the osmotic molecular weight of the dissolved substance, but it has proved impossible up to the present to establish any connection. (*See* Frankland and Pickard, Chem. Soc. Trans. 1896, 69, 131; Patterson, *ibid.* 1901, 79, 182; 1902, 81, 1111; Ber. 1905, 38, 4049; 1908, 41, 113; Patterson and Thomson, *ibid.* 1907, 40, 1244; Walden, *ibid.* 1905, 38, 389; 1906, 39, 658; 1907, 40, 2463; Purdie and Irvine, Chem. Soc. Trans. 1904, 85, 1055.)

From the point of view developed in the preceding part of this article it is not difficult, in a proximate sense, to account for this concentration effect. In nitrobenzene, for example, since dilution raises the maximum in the T-R curve, and also displaces it towards the left of the diagram, it is natural that at some fixed temperature such as 20° the rotation should gradually increase with increasing dilution to give a C-R curve, which is simply an expression of the manner in which the general T-R curve is shifted by that solvent. If the general curve is very rapidly displaced, then it might be that the C-R curve would show a maximum, as is actually the case for ethyl tartrate in quinoline. The C-R curve for ethyl tartrate in benzaldoxime shows a similar behaviour, but here the matter has not been sufficiently well investigated to allow of a definite judgment.

Another proposal, originally made by Tammann, was that the rotation depends upon the internal pressure of the solvent or of the mixture of solute and solvent. Actually to determine the influence of pressure on rotation is very difficult, since the pressure applied to the liquid must also be applied to the end discs of the containing tube, when they too become double refracting and optically active. In the one investigation which has been carried out on the subject, L. H. Siertsema (Arch. Néerl. Sci. 1899, [ii.] 2, 29; 1900, [ii.] 3, 79) found it necessary to immerse the polarising and analysing prisms in the liquid to be examined and submit them as well as the liquid to the pressure. It was found, for instance, that the rotation, 12·4°, of a decimetre layer of a cane sugar solution $c=18{\cdot}7$, was only altered by about 0·31° per one hundred atmospheres increase of pressure. (These figures are calculated from the numbers in the tables given by Siertsema.) This idea was applied by Patterson (Chem. Soc. Trans. 1901, 79, 188) in the case of ethyl tartrate in various solvents, but instead of calculating the internal pressure, the molecular solution-volume of the ethyl tartrate at infinite dilution in the different solvents was determined, the assumption being made, as a first approximation, that all the change of volume suffered in the process of solution might be attributed to the solute, and further, that the magnitude of the solution-volume might be regarded as a measure of the internal pressure. Although these assumptions are not generally admissible, it is nevertheless possible that in some instances they may be nearly fulfilled. In any case experiment discovered a parallelism between the magnitude of the specific rotation and the molecular solution-volume, both estimated at infinite dilution, as is illustrated in the following table (Ber. 1905, 38, 4101):

Table X.—Rotation and Solution-Volume of Ethyl Tartrate in Various Solvents.

(Ethyl tartrate, M.V.=170·9 c.c.)

Solvent	[M.S.V.]^{20} infinite dilution	$[\alpha]_D^{20}$ infinite dilution
Water . .	160·1	+26·85°
Methyl alcohol .	159·3	+11·50
Glycerol . .	163·3	+10·57
Ethyl alcohol .	164·0	+9·13
n-Propyl alcohol	167·5	+7·40
iso-Butyl alcohol	170·3	+6·53
sec-Octyl alcohol	174·3	+5·24
Benzene . .	175·1	+6·1
Toluene . .	174·8	+4·6
o-Xylene . .	176·8	+2·7
m-Xylene . .	176·5	+1·8
p-Xylene . .	176·1	+0·7
Mesitylene .	177·4	−3·0
Chloroform .	178·0	−3·2

Except in the case of water, there appears to be a fairly close relationship between the values of these two magnitudes. The idea was taken up by Winther and applied to explain the change of rotatory power with variation of temperature. In certain cases it is found that there is a direct, linear relationship between the values of the rotation and the molecular volume either in the homogeneous condition or in solution. Thus, for example, the figures for homogeneous ethyl diacetyltartrate may be given:

Table XI.

t	$[\alpha]_D$	$\Delta[\alpha]_D$	v	Δv	k
56·8°	+4·37°		0·8906		
		0·38		0·0087	44
67·6	4·75		0·8993		
		0·17		0·0027	63
71·3	4·92		0·9020		
		0·28		0·0061	46
78·2	5·20		0·9081		
		0·40		0·0070	57
86·7	5·60		0·9151		
		0·70		0·0114	61
100·0	6·30		0·9265		

In the above table v is the specific volume, and k is a constant calculated from the equation:

$$\Delta[\alpha]_D = k\Delta v$$

The values of k vary irregularly about a mean value of 54, so that the rotation appears to be directly proportional to the specific volume. (For many other examples, *see* Winther, Zeitsch. physikal. Chem. 1906, 55, 263.)

The following table gives some data for ethyl tartrate and for nicotine, in regard to the relative effect of the same set of solvents on the rotation of a number of different active compounds:

Table XII.

Solvent	Ethyl tartrate $[\alpha]_D$ infinite dilution	Nicotine $[\alpha]_D$ infinite dilution
Formamide .	+30·4°	−70°
Water . .	26·85	77·4
Methyl alcohol .	11·5	129·4
Ethyl alcohol .	9·13	140·1
Benzene . .	6·1	163·5
Ethylene bromide	−19·1	183·5

The sequence of the rotations in these different solvents is the same for both active compounds. *See also* Walden (Ber. 1905, 38, 345) for data bearing on this subject. Further work in this direction is desirable.

Rotation dispersion.—The determination of rotation for light of different wave-lengths may be carried out either with sources of light approximately monochromatic, such as flames containing incandescent salts of sodium, lithium, thallium, indium; or with a mercury or cadmium arc lamp, the light being purified by means of some coloured solution which absorbs the rays not required. (*See*, for example, Winther, Zeitsch. physikal. Chem. 1902, 41, 161; Scheuer, *ibid.* 1910, 72, 513.) It is, however, better to purify white light or that from any of the sources mentioned, by means of a spectroscope, placed at either end of the polarimeter.

A photographic method of determining dispersion into the ultra-violet has been described by Lowry (Proc. Roy. Soc. 1908, A. 81, 472; Chem. Soc. Trans. 1915, 107, 1179).

Results similar to the following are then obtained:

Fraunhofer line	B	C	D	E	F	G
Wave-length [$\mu\mu : 10^{-7}$ cm.]	686·7	656·2	589·2	526·9	486·1	430·7
Quartz [1] α [1 mm.]	+15·75°	17·31°	21·71°	27·54°	32·76°	42·59°
Sucrose [2] [α]	+47·56	52·70	66·40	84·56	101·81	131·96

The ratio of the values for light of any two wave-lengths is often termed the dispersion coefficient, and in the above cases, taking the B line as standard, the dispersion coefficients would be as follows:

Fraunhofer line	B	C	D	E	F	G
Quartz . .	1	1·09	1·38	1·75	2·08	2·70
Sucrose . .	1	1·11	1·40	1·78	2·13	2·77

The dispersion of quartz is practically the same as that of a cane sugar solution—a sucrose solution which has the same rotation as a certain quartz plate for any one ray will have practically the same rotation as the quartz plate for all rays and for all concentrations, which makes it possible to use quartz wedge compensation instruments for the determination of the rotation of sugar solutions.

Biot thought that the rotation was inversely proportional to the square of the wave-length of the light used. Boltzmann (Pogg. Ann. Jubelb. 1874, 128) proposed the equation

$$\alpha = \frac{A}{\lambda^2} + \frac{B}{\lambda^2}$$

in which, from the above observations on quartz, $A = 7{\cdot}108293 \times 10^{-6}$ and $B = 0{\cdot}1477086 \times 10^{-12}$, whilst for the sugar solution $A = 2{\cdot}16036 \times 10^{-5}$ and $B = 5{\cdot}47276 \times 10^{-13}$. Winther (Zeitsch. physikal. Chem. 1902, 41, 182) suggests another expression, which agrees better with his results for esters of tartaric acid and has the merit of including temperature as a parameter.

Drude has suggested an expression of the form

$$\alpha = \frac{k_1}{\lambda^2 - {\lambda_1}^2} + \frac{k_2}{\lambda^2 - {\lambda_2}^2} + \ldots$$

This has been advocated by Lowry, who finds the behaviour of quartz to be represented by the equation

$$\alpha = \frac{k_1}{\lambda^2 - {\lambda_1}^2} + \frac{k_2}{\lambda^2 - {\lambda_2}^2} + \frac{k}{\lambda^2}$$

[1] Soret and Sarasin, Compt. rend. 1882, 95, 635.
[2] Cane sugar in water, $p = 10$–30, Stefan, Wien. Sitz. Ber. 1866, 52, ii. 486.

in which ${\lambda_1}^2 = 0{\cdot}010627$, ${\lambda_2}^2 = 78{\cdot}22$ (Lowry and Dickson, Chem. Soc. Trans. 1913, 103, 1067).

In the majority of cases which had been examined until recently, the dispersion curves approximated to rectangular hyperbolæ, and this behaviour was consequently regarded as normal. But in some, seemingly exceptional, instances, as was first observed for solutions of tartaric acid by Biot (Mém. de l'Acad. 1838, 15, 93), the magnitude of the rotation does not increase constantly as the wave-length of the light used diminishes, but reaches a maximum at some intermediate wave-length and then decreases again, which, although it will probably

Rotation Dispersion of Methyl, Ethyl and n Propyl Tartrate at Different Temperatures.

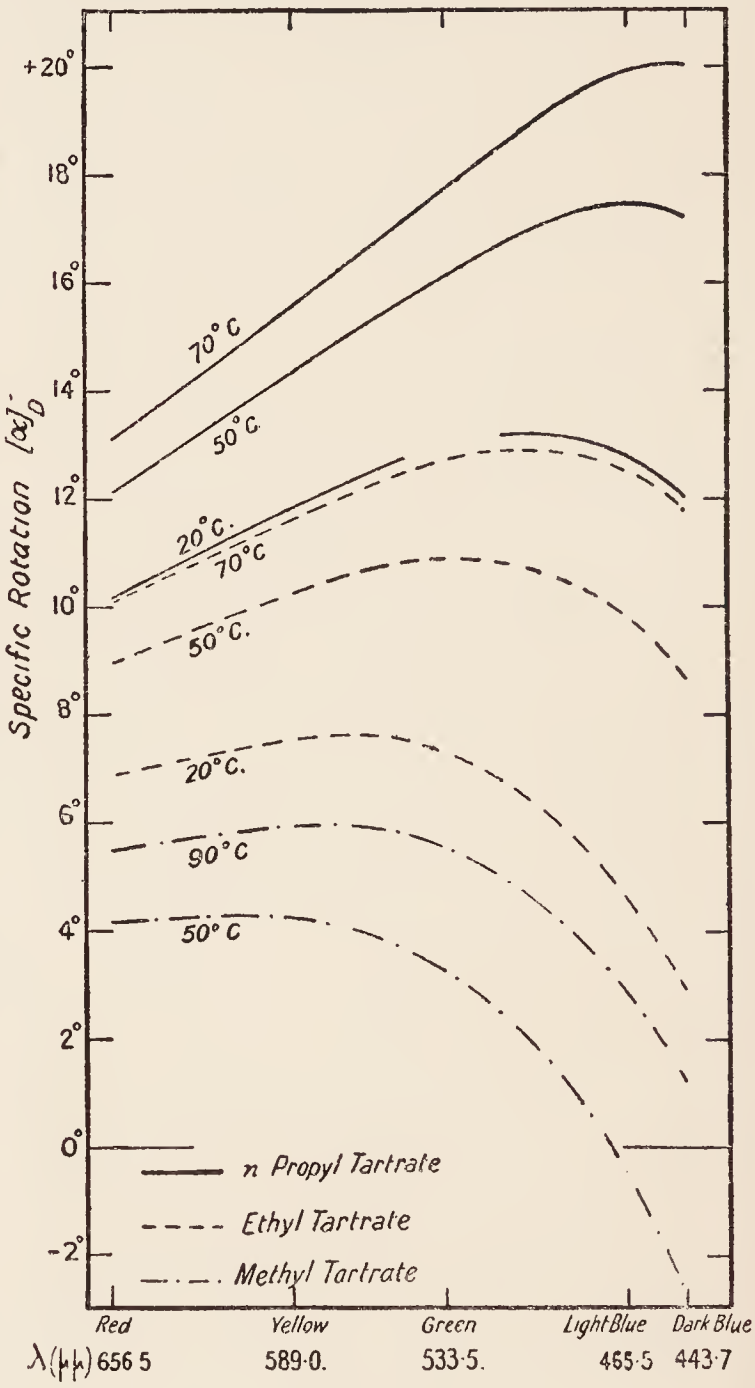


FIG. 38.

prove to be the general behaviour, has been termed *anomalous rotation-dispersion.* Winther (Zeitsch. physikal. Chem. 1902, 41, 177) finds this to occur also in homogeneous compounds, such as the methyl, ethyl and *n*-propyl esters of tartaric acid, and the same holds for ethyl diacetyltartrate (Scheuer, *ibid.* 1910, 72, 587).

Fig. 38 represents data obtained by Winther *l.c.*) for the first three simple esters of tartaric acid, at a number of different temperatures, the dispersion being visibly anomalous in all cases, a maximum occurring in the visible spectrum. The maximum rotation for methyl tartrate occurs in the neighbourhood of the

yellow light, but as the temperature rises the maximum shows a tendency to shift towards the violet; this is clearly more pronounced amongst the curves for ethyl tartrate, and still more so in those for *n*-propyl tartrate. It is of interest that, just as has already been observed in regard to the effect of temperature change on rotation in solution (Fig. 36), the set of curves for these three homologous esters seems to form a complete whole; some property appears to progress gradually throughout the diagram, irrespective of the nature of the chemical compound used. The alteration of dispersion for the three esters is closely analogous, so that if methyl tartrate be heated until it has a rotation of, say, $\alpha°$ for the red rays, its dispersion curve at that temperature will be almost the same as that for ethyl tartrate at the temperature at which its rotation is also $\alpha°$ for red light, practically the same curve being obtained for *n*-propyl tartrate at some other temperature. The dispersion curve for ethyl tartrate, for example at 72°, is nearly coincident with the dispersion curve for *n*-propyl

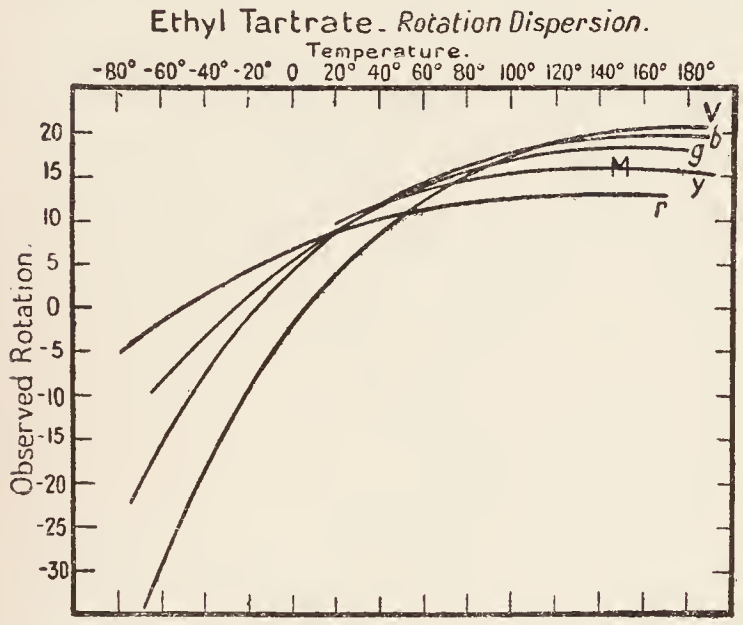


Fig. 39.

tartrate at 19°; so far as this property is concerned, ethyl tartrate at 72° seems to be much the same thing as *n*-propyl tartrate at 19°.

It is clear that in these curves the maximum which constitutes the anomalousness tends to pass from the red at low temperatures to the violet at high temperatures, and may easily pass so far in either direction as to yield, in the visible, a curve almost indistinguishable from that which is claimed to be characteristic of a 'normal' substance.

Lowry proposes to divide dispersion curves into two classes, simple and complex, the former being such as can be represented by a Drude expression of the simplest form:

$$a = \frac{k}{\lambda^2 - \lambda_0{}^2}$$

(Lowry and Dickson, Chem. Soc. Trans. 1913, 103, 1068); the latter such as require for their representation an expression containing two or more terms (Lowry, *ibid.* 1915, 107, 1196).

But the phenomena of rotation dispersion are perhaps best considered from the point of view of the T-R curves. This may be illustrated from Fig. 39, which shows the T-R curves for ethyl tartrate over a fairly wide range of temperature. The values of the intercepts of these curves by any ordinate when plotted against the corresponding wave-length of the light will give the ordinary dispersion curve. It is to be noticed that the T-R curves shown do not intersect all at one point, but over a range of temperature, thus forming an envelope, and it is evident that in this region the dispersion is visibly anomalous. The dispersion curves corresponding to the extreme ends of the diagram, however, may not be visibly anomalous, but whether they are likely ever to become normal in any absolute sense is doubtful. It is certainly clear that if the T-R curves intersect over a range of temperature, however slight, the dispersion must be anomalous at least in that neighbourhood.

Whether it is possible for the T-R curves to intersect all at one point is not definitely known. If it were possible the point of intersection might perhaps necessarily be at zero rotation. Conceivably those intersecting over a range would show always anomalous rotation dispersion, whilst those meeting at a single point would show normal rotation dispersion; but on the subject little is definitely known.

It has already been mentioned that the effect of solution is, usually, to displace the maximum in the T-R curves to one side or the other of the diagram. It has also been shown in most or all of the cases examined in this connection, that the point of intersection of any two given T-R curves is displaced (laterally) in much the same way as the maximum. Thus since both the maximum and the point of intersection are analogously displaced it would seem that the displacement is suffered by the T-R curve as a whole. It appears, however, also to be the case that whereas the value of the maximum rotation is very different in different solvents or for related compounds, the value of the rotation at which a given pair of T-R curves intersect varies but little under varied circumstances, although the temperature of intersection may be entirely altered. This is perhaps the most significant fact yet observed in regard to optical activity. It will be referred to again in connection with Armstrong and Walker's Characteristic Diagram.

In spite of the fact that very little is known as to the phenomena characteristic of normal rotation-dispersion—even a satisfactory definition being lacking—Armstrong and Walker have recently attempted to account for the phenomena of anomalous rotation-dispersion—which there is meantime no good reason to suppose radically different from normal rotation-dispersion—by reviving a suggestion originally made by Arndtsen (Ann. Chim. 1858, [iii.] 54, 403), and based on some observations of Biot, namely that these phenomena are due to the existence of two, or more, dynamically isomeric forms of the active compound, the assumption being that these have opposite rotations and different dispersions. Although the mechanism suggested is open to serious criticism (Chem. Soc. Trans. 1916, 109, 1204), it led Armstrong and Walker to the construction of what they term Characteristic Diagrams, in which data for different related active compounds under varied circumstances as to temperature, solvent and concentration may be grouped together, and which show, in a striking manner, that in place of the apparent lack of any connection between the different phenomena relating to

optical activity there is in fact a deep-seated uniformity of behaviour.

Fig. 40 shows one of these characteristic diagrams plotted in the manner suggested by Patterson, and representing some results obtained by Pickard and Kenyon, for methyl-*tert*butylcarbinol. In this diagram values for mercury green are supposed to be marked off along the horizontal axis. Immediately below each of these points are then plotted the *differences* between the rotations for Hg$_g$ and Na$_g$, and immediately above them the differences between the rotations for Hg$_g$ and Hg$_v$. It will be seen that the points lie approximately along three straight lines which meet at, or very nearly at, a point. Thus it is to be expected that if under some special circumstances, of temperature, or solvent, or concentration, the specific rotation for green were to become −1°, the rotation for sodium yellow and violet would likewise become −1°. The actual rotation at any point on the diagram is the horizontal distance from the point of intersection of the axes plus the vertical distance from the horizontal axis. Pickard and Kenyon (Chem. Soc.

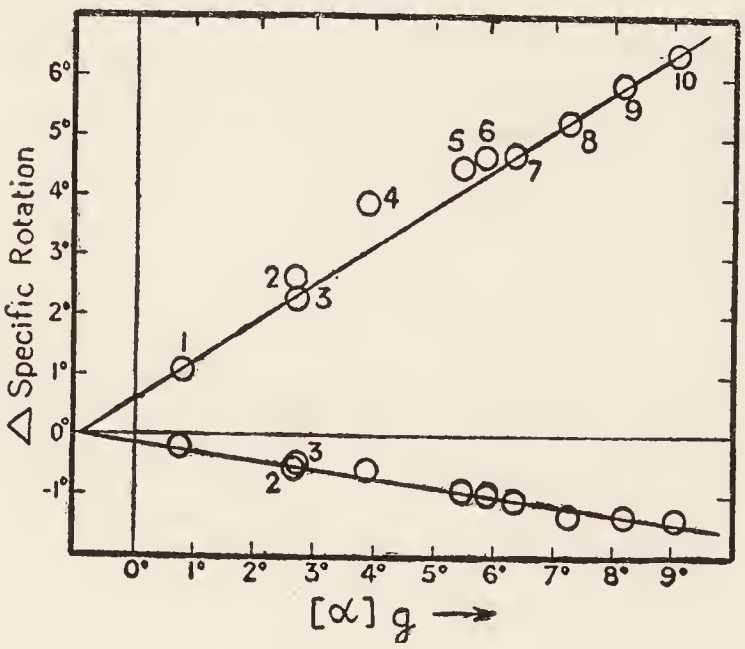


Fig. 40.

Trans. 1915, 107, 115, and earlier papers) have shown that in very many cases, the data they have obtained fit, in a most interesting manner, on to characteristic diagrams.

This point at which any two, or more, lines on a characteristic diagram meet is likely to prove of special significance in the development of the theory of optical activity. It is, as a little consideration will show, the rotation value (referred to above) at which the T-R curves for the colours in question for any of the compounds represented in the diagram in any solvent, at any concentration, would cut one another, and, as has been pointed out by Patterson, if dispersion ratios, instead of being calculated in the ordinary fashion, be calculated with respect to this point as a rational zero, values are then obtained which are in fact sensibly constant over a very considerable range of temperature. It is, however, hardly to be expected that the dispersion for a given compound can ever be an absolute constant (Chem. Soc. Trans. 1916, 109, 1176).

As has already been pointed out, the effect of temperature change or of solvent influence is apparently to bring into view different regions of a general curve. It is known that, at least in certain cases, the T-R curves for the different colours intersect, and this appears to occur in the neighbourhood of the points of inflection between maximum and minimum values. It becomes of interest to ascertain whether intersection always takes place between maximum and minimum values.

The question has been investigated by methods similar to those referred to above. The T-R curves of a set of related active compounds may be displaced to one side or the other either by change of temperature or by the use of suitable solvents, and the extended general curves thus arrived at. The graphs of Fig. 41 represent in a purely qualitative fashion the results so far obtained for the tartrates. At low temperatures there seems to be a deep minimum of low rotation value (Proc. Roy. Soc. Edin. 1918–19, 39, 18). At a higher temperature the T-R curves intersect, producing visibly anomalous rotation dispersion, after which a maximum is reached. The graphs then, without intersection, descend to pass through another minimum, subsequently rising again, also apparently without intersection, to a new maximum which has not yet been investigated.

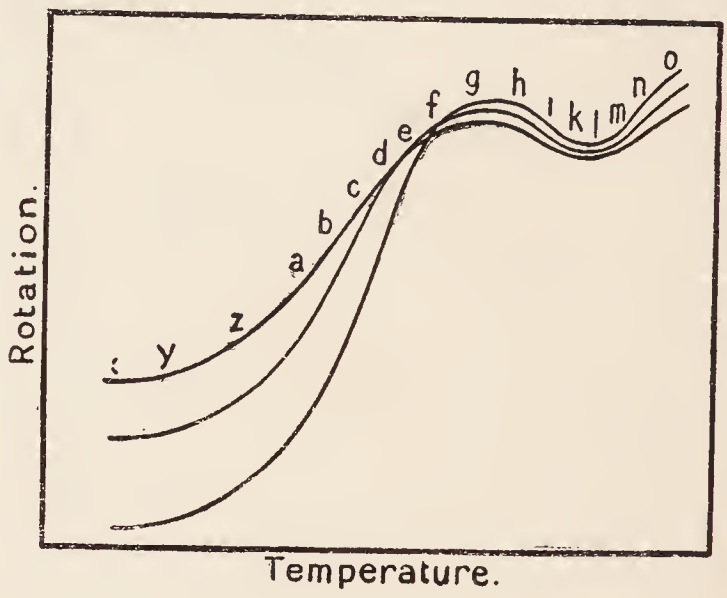


Fig. 41.

Rotation of active salts in solution.—In 1873, Landolt (Ber. 1873, 6, 1077) observed that some of the neutral tartrates in aqueous solution had all very nearly the same specific rotation, whilst, later, Oudemans (Annalen, 1879, 197, 48, 66) showed that the rotation of dilute solutions of salts of quinamine seemed to be independent of the acid radicle. Hädrich (Zeitsch. physikal. Chem. 1893, 12, 476) applied the dissociation theory to the explanation of these results, suggesting that, as the solution of a salt is diluted, the rotation is modified because the active radicle becomes more and more dissociated from, and therefore less and less influenced by, the inactive radicle. In very dilute solutions, the rotation is that, merely, of the free active ion. Thus Landolt found the following data for solutions containing 7·69 grms. of tartaric acid in 100 c.c. Even in these by no means very dilute solutions the rotations lie fairly close together.

Neutral tartrate of	$[M]_D$
Lithium . . .	+58·1°
Sodium . . .	59·9
Potassium . . .	64·4
Ammonium . . .	63·0

Again, Pope and Peachey (Chem. Soc. Trans. 1899, 75, 1086) give the following rotations for compounds formed by the combination respectively of dextro- and lævo- tetrahydroquinaldine with dextro-camphor-sulphonic acid.

Substance	$[M]_D$
$d C_{10}H_{13}N \cdot d C_{10}H_{15}O \cdot SO_3H$	$+173{\cdot}3°$
l ——— l ———	$-69{\cdot}5$

Half the difference between these, 121·4°, should be the rotation of a dilute solution of either form of tetrahydroquinaldine hydrochloride, and for the lævo variety experiment gave −121·7°. Further, half the sum of the above, 51·9°, should be the rotatory power of ammonium camphor sulphonate, for which the value 51·7° was found. Use is occasionally made of this principle in determining the rotation of small quantities of active bases or acids, obtained by the resolution of potentially active compounds.

The truth of this Law of Oudemans, as it is called, has been questioned by F. L. Shinn (J. Phys. Chem. 1907, 11, 201).

Mixed solvents.—The effect of mixed solvents such, for instance, as a mixture of nitrobenzene and ethylene bromide on ethyl tartrate, or of water and calcium chloride on glucose, has been examined by Rimbach (Zeitsch. physikal. Chem. 1892, 9, 698); Rimbach and Weber (*ibid.* 1905, 51, 473); Patterson and Montgomerie (Chem. Soc. Trans. 1909, 95, 1128); Stubbs (*ibid.* 1911, 99, 2265); Patterson and Anderson (*ibid.* 1912, 101, 1833), but no generalisation seems to be possible as yet.

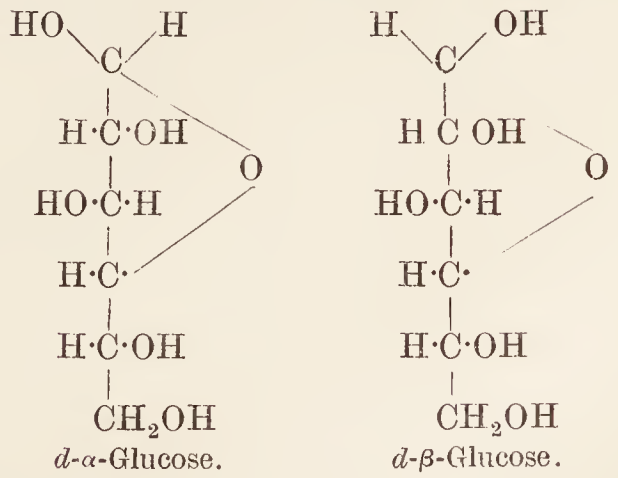
Combination of Active Solute with Inactive Solvent.

A suggestion often made to account for the variations of rotation observed in solution in what are termed 'indifferent' solvents, is that complex molecules of solute and solvent are formed, but the evidence advanced is usually of a negative character. An extensive research by Scheuer (Zeitsch. physikal. Chem. 1910, 72, 513), which included experiments on the viscosity, dilatation, melting-point, and rotation for light of various refrangibilities, of mixtures of ethyl diacetyltartrate, and menthol respectively, with a number of different solvents, failed to detect, either in the liquid or the solid phase, any sign of complex formation.

In some cases, however, combination probably does occur. Thus Biot (Mém. de l'Acad. 1837, 16, 229; Ann. Chim. 1844, [iii.] 11, 82; 1850, 29, 341, 430; 1860, 59, 229) noticed that the addition of boric acid to solutions of tartaric acid greatly increased their rotation, and the same thing has been observed by Gernez for molybdates and tungstates (Compt. rend. 1887, 104, 783; 1888, 106, 1527; 1889, 108, 942). The addition of one molecular proportion of ammonium molybdate $[NH_4]_6Mo_7O_{24},4H_2O$, to a $c=2{\cdot}5$ solution of tartaric acid, raises the rotation, α_D^{17}, from $+0{\cdot}351°$ to $+15{\cdot}66°$. This principle is therefore occasionally employed in investigations where small quantities of active compounds are obtained, in order to increase the rotation and render it perceptible. These increases have only been observed for active oxy-acids, and the method must be used with caution, since it was found by Gernez (Compt. rend. 1889, 109, 769) that whilst the addition of one molecular equivalent (2·017 grms.) of sodium molybdate, $Na_2MoO_4,2H_2O$ to malic acid solution, $c=9{\cdot}97$, raised α_D^{17} from $-0{\cdot}189°$ to $+13{\cdot}26°$, the addition respectively of 1·4, 2·85, 4·25 grms., gave in each instance an inactive solution, maximum and minimum rotations occurring at intermediate concentrations. Compounds of this type and also those containing arsenic and antimony have been examined by G. G. Henderson with Prentice (Chem. Soc. Trans. 1895, 67, 1035), Barr (*ibid.* 1896, 69, 1452) and Orr and Whitehead (*ibid.* 1899, 75, 548) not only with malic acid but also with lactic acid, whilst Walden (Ber. 1897, 30, 2889) uses alkaline uranyl nitrate for producing strongly active compounds of the same type.

Muta-rotation.—It not infrequently happens that the rotation of a compound, generally in solution, starting from a certain initial value gradually falls to reach a different end value. The substances which first attracted attention in this direction belong to the class of sugars, which rendered the matter of practical importance. When *d*-glucose is crystallised from 70 p.c. alcohol at the ordinary temperature, an anhydrous product is obtained, giving when dissolved in water, an initial rotation of about $[\alpha]_D=+109°$ which falls gradually to the constant value +53°. The solid form is called *d*-α-glucose. If, on the other hand, glucose be crystallised from water at a temperature above 98°, a solid, *d*-β-glucose, separates having a rotation initially of only $[\alpha]_D=+19°$ or thereabouts, the value being a little uncertain, as the substance is difficult to prepare in a pure condition. This rotation, too, changes slowly with lapse of time and ultimately also acquires the value +53°. Since the final rotation is almost half the highest value the phenomenon used to be called bi-rotation or semi-rotation, but is now generally referred to, on the suggestion of Lowry, as muta-rotation (Chem. Soc. Trans. 1899, 75, 213). A similar behaviour is found for fructose, galactose, lactose, maltose, and other sugars.

The two varieties of glucose in the solid condition may be represented by the formulæ:

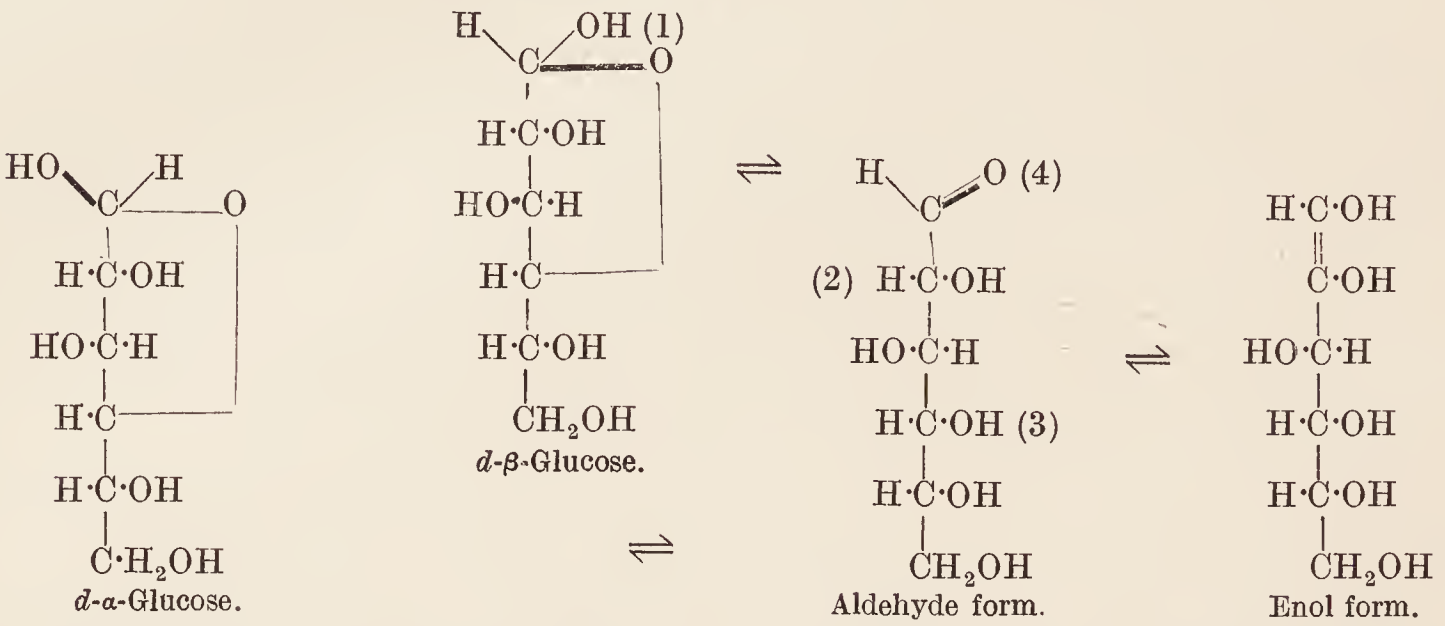


d-α-Glucose. *d*-β-Glucose.

in which, however, the relative positions of the hydrogen atom and the hydroxyl group attached to the uppermost carbon atom are not definitely known.[1] When one of these compounds is

[1] In regard to this subject in general, *see* E. F. Armstrong: The Simple Carbohydrates and the Glucosides, 3rd Ed. (Longmans, 1919).

dissolved in water a change might take place in two essentially different ways. Emil Fischer (Ber. 1890, 23, 2626) suggested that the molecule may become hydrated, the final constant value of the rotation being that of the hydrate. Lowry, however (Chem. Soc. Trans. 1899, 75, 213; 1904, 85, 1541, 1551), from analogy with the rotation changes which take place in nitrocamphor in non-aqueous solutions, in which there can be no hydration, attributes the change to an isodynamic process or perhaps to two such processes:



In solution the compound of constant rotation may have the true aldehyde formula or it might have the enolic structure, the presence of which last seems necessary to account for the readiness with which glucose in faintly alkaline solution is converted into a mixture of glucose, fructose and mannose. On dissolving *d*-β-glucose in water, the hydrogen atom marked (1) may wander to the lactonic oxygen atom, the uppermost carbon atom of the *d*-β-glucose molecule thus losing its asymmetry to give the inactive group $\begin{matrix} H\cdot C=O \\ | \end{matrix}$ of the aldehyde form. If now this hydrogen atom pass back again from its position (3) and attach itself to the aldehyde oxygen atom (4) by the bond indicated by the thick line, it will yield *d*-α-glucose, in which the asymmetry of the uppermost carbon atom is the opposite of that found in *d*-β-glucose. If the hydrogen atom (2) of the aldehyde form wander to the oxygen atom (4), both of the upper carbon atoms lose their asymmetry and the enolic form results, which presumably may pass back again through the aldehyde form into *d*-α-glucose or *d*-β-glucose or into the two forms of fructose or mannose respectively.

Magnetic rotation.—Faraday discovered in 1845 (Phil. Trans. 1846, 1) that the plane of polarisation of light passed through transparent matter of any kind in a magnetic field in the direction of the lines of force, is altered to an extent proportional to the strength of the field, the thickness of the layer of substance traversed, and the nature of the light used. If the field is produced by a current flowing round a coil, the direction of rotation of the plane of polarisation is generally positive for diamagnetic substances and negative for magnetic substances, the positive direction being that in which the current producing the field flows, without reference to the direction of the ray. Thus if the field be produced by a current flowing in the counter-clockwise direction relative to the observer, the rotation of a positive substance will be also in a counter-clockwise direction, and if the beam be reflected back through the substance the plane of polarisation will be again deflected in the same direction as before, so that the angle of rotation after passing back and forwards through the substance will be doubled. Magnetic rotation thus differs very markedly from permanent rotation. See note (1), p. 338.

From the chemical point of view this phenomenon has been developed almost exclusively by the late Sir W. H. Perkin, in a series of very comprehensive papers (Chem. Soc. Trans. 1882, 41, 330; 1884, 45, 421; 1896, 69, 1025; 1906, 89, 608; 1907, 91, 806, and others).

Perkin's method consists in determining the magnetic rotation of water and then under the same circumstances of field, &c., the magnetic rotation of some other substance, the current being reversed after each observation and the mean of the sum taken. Each rotation is then divided by the corresponding density, the value thus found for the substance as compared with that for water taken as unity, being the specific magnetic rotation of the substance. The specific rotation multiplied by the molecular weight gives the molecular magnetic rotation.

In ascending a homologous series, the molecular magnetic rotation increases by a constant amount for each CH_2 group added, and definite values may be obtained for certain groups or atoms so that, knowing the constitution of a compound, its molecular magnetic rotation can be calculated. Perkin applied this method as a criterion for the determination of the constitution of certain substances which presented difficulty. Thus, for example, he found (Chem. Soc. Trans. 1902, 81, 294)

Substance	Molecular magnetic rotation
Hexane . . .	6·646
Hexamethylene . .	5·664

the difference between these values (−0·982) being that due to ring formation and loss of two atoms of hydrogen. In his last paper (*ibid.* 1907, 91, 807) he quotes:

Magnetic rotation of hexatriene .	12·196
Difference due to ring formation .	−0·982
	11·214

The sum, 11·214, should be the rotation of benzene, which is, in fact, 11·284. There is little doubt that magnetic rotation is one of the most definitely constitutive properties that we know, but, owing to the elaborate and costly character of the apparatus required and the unremitting attention necessary in carrying out observations, it has been used by few other workers. T. S. P.

POLIANITE. Manganese dioxide MnO_2 crystallised in the tetragonal system. Crystals are rare and usually very indistinct, so that the mineral is not readily distinguished from pyrolusite (*q.v.*). It differs, however, in its much greater hardness (H.=6–6½); it scratches glass and does not soil the fingers. Sp.gr. 4·9–5·0. Like pyrolusite, it has a greyish-black colour with metallic lustre, and often occurs as a pseudomorph after manganite. The mineral is known only from Platten in Bohemia. It is probably of more frequent occurrence in the mixed black oxide ores of manganese than has been hitherto recognised. L. J. S.

POLLUCITE or **POLLUX.** Acid silicate of cæsium and aluminium, $H_2Cs_4Al_4(SiO_3)_9$, crystallised in the cubic system. It is the only mineral containing cæsium as an essential constituent; analyses show Cs_2O 30·0–36·8 p.c., with small amounts of potassium, sodium, and lithium in isomorphous replacement, but only traces of rubidium. The composition is analogous to that of leucite, $KAl(SiO_3)_2$, with the addition of $\frac{1}{4}H_2SiO_3$, and also of analcite

$$Na_2Al_2(SiO_3)_4, 2H_2O,$$

both of which minerals present a certain external resemblance to pollucite. Crystals are rough and usually much corroded. The material is colourless and clear with a glassy appearance and usually much fissured. It is very brittle with a conchoidal fracture and no cleavage. Sp.gr. 2·87–2·98; H.=6½. The mineral is found in granite-pegmatite at San Piero in Campo on the Island of Elba, and at several places (Hebron, Rumford, Paris, and Buckfield) in Maine, U.S.A. Crystals from Elba measure up to 5 cm. across, and masses 24 cm. across have been found in Maine. L. J. S.

POLONIUM (*Radium F*; *Radiotellurium*). At.wt.=approx. 210 (?).

A radioactive element, discovered by P. and M. Curie in the residues obtained from pitchblende after the mineral had been roasted with sodium carbonate and the product extracted with sulphuric acid to dissolve uranium salts. The insoluble residue, from which radium was originally prepared, was found to contain another radioactive element which was precipitated together with bismuth sulphide by hydrogen sulphide in acid solution (Compt. rend. 1898, 127, 175). The further separation of the active body from bismuth was effected by the following methods: (1) sublimation of the sulphides at 700° *in vacuo*, the active sulphide being the more volatile; (2) precipitation of the basic nitrates from solution, the above material precipitating first; (3) precipitation of a strongly acid chloride solution with hydrogen sulphide, the active sulphide separating first. (For the preparation of polonium compounds *v.* also Giesel, Ann. Chim. 1899, [ii.] 69, 91; Ber. 1902, 35, 3608; 1903, 36, 728, 2368; 1908, 41, 1059; Marckwald, Ber. 1902, 35, 2285; Curie and Debierne, Compt. rend. 1910, 150, 386.)

In 1902, Marckwald (Ber. 1902, 35, 2285, 4239; 1903, 36, 2662) obtained a radioactive substance associated with tellurium, which he called *radiotellurium*. This is almost certainly identical with polonium, as Debierne soon afterwards pointed out (Compt. rend. 1904, 139, 281). Although Marckwald (Jahrb. Radioaktiv. Elektronik. 1905, 2, 133) disputed their identity, he subsequently (Chem. Zentr. 1906, ii. 412) recommended that his material should be called polonium.

Polonium has been found in the uranium mineral carnotite (Friedel and Cumenge, Compt. rend. 1899, 128, 532).

When a plate of bismuth is immersed in a polonium solution, the active matter is deposited on the plate; the active material is also precipitated by stannous chloride (Marckwald).

The radiation from polonium is extremely active, consisting entirely of α-rays identical with those of radium (Becquerel, Compt. rend. 1903, 136, 431, 977; Lawson, Chem. Zentr. 1920, iii. 431). The rays are deflected in a strong magnetic field (Mackenzie, Phil. Mag. 1905, [vi.] 10, 538; Ewers, Chem. Zentr. 1906, i. 1084). The range of the α-particles in air is 3·8 cms. (Levin, Amer. J. Sci. 1906, [iv.] 22, 8; *cf.* Aschkinass, Annalen Physik. 1908, [iv.] 27, 377). The activity of polonium decays according to the usual exponential law, the half-period being 140 days (Curie, Compt. rend. 1906, 142, 273); 136·3 days (von Schweidler, Ber. Deut. physikal Ges. 1912, 14, 536; Curie, Phys. Radium, 1920, [vi.] 1, 12). The half-period for radiotellurium is 139·6 days (Greinacher and Herrmann, Jahrb. Radioaktiv. Elektronik. 1905, 2, 136).

Owing to the minute quantities of polonium available it has been extremely difficult to detect helium as one of its disintegration products, but Curie and Debierne (Compt. rend. 1910, 150, 386) have obtained 1·3 c.mm. of helium from approximately 0·1 mgm. of polonium (*cf.* Greinacher and Kernbaum, Zeitsch. physikal. Chem. 1907, 8, 339). The spectrum lines λ=4642, 4170·5, 3913·6, 3652·1 probably belong to polonium. Polonium preparations slowly evolve heat (Duane, Compt. rend. 1909, 148, 1665).

Polonium has been identified with radium F, the last of the series of transformation products of radium that has been recognised. The change from radium to radium F involves the loss of four α particles from the atom. The atomic weight of polonium should therefore be about 210. The unknown radium G, into which polonium disintegrates, is devoid of sensible radioactivity, since the half period of polonium preparations that have been kept for five years is practically identical with the figure given above (Waters, Phil. Mag. 1910, [vi.] 19, 905). Radium G will probably prove to be lead. Lawson and independently Paneth have inferred the existence of a gaseous hydride of polonium.

The *radio-lead* of Hofmann and Strauss (Ber. 1901, 34, 3033; Hofmann and Wolff, *ibid.* 1903, 36, 1040) has been shown to owe its activity to the presence of the transformation products *radium D*, *E*, and *F*. The substance *β-polonium*, described by Giesel (Ber. 1906, 39, 780), was

shown later to be radium E (Giesel, *ibid.* 1906, 39, 1014; *cf.* Paneth and Hevesy, Monatsh. 1913, 34, 1605; 1915, 36, 45).

POLYBASITE. A sulphantimonite of silver (60–72 p.c.) and copper (3–15 p.c.) with the formula $8(Ag,Cu)_2S\cdot(Sb,As)_2S_3$ (F. R. Van Horn, Amer. J. Sci. 1911, 32, 40). The antimony may be partly or wholly replaced by arsenic, forming a passage to the isomorphous species *pearceite*: small amounts of zinc and iron are also often present. Both minerals occur as iron-black, six-sided plates with monoclinic symmetry. They are found in the silver-mining districts of Mexico, Colorado, Nevada, &c., sometimes in sufficient abundance to be of importance as ores of silver. L. J. S.

POLYCHREST SALT. An old name for normal potassium sulphate; applied also sometimes to Rochelle salt.

POLYCHROMINE *v.* PRIMULINE AND ITS DERIVATIVES.

POLYCRASE. A rare-earth mineral consisting of hydrated columbate and titanate of yttrium (Y_2O_3 13–27 p.c.), erbium (Er_2O_3 0–8 p.c.), cerium (Ce_2O_3 0–3 p.c.), and uranium (UO_2 5–19 p.c.). It is closely related to euxenite (*q.v.*), from which it differs in containing more titanium and less columbium. The rough orthorhombic crystals are also very similar to those of euxenite. On the fresh conchoidal fracture it is black with a brilliant pitchy lustre; thin splinters are transparent and brownish in colour. Sp.gr. 4·97–5·04; H.=5–6; decomposed by strong sulphuric acid. The mineral is found in pegmatite-veins at several places (Hitterö, Arendal, Moss, Evje, Iveland) in the south of Norway; at Slättåkra in Sweden; in the gold-quartz vein of La Gardette in Isère; near Dresden; in North and South Carolina; and at Calvin in Ontario. L. J. S.

POLYDYMITE. A nickel sulphide, Ni_4S_5 or Ni_3FeS_5, crystallised in the cubic system. It forms octahedra, which are repeatedly twinned (hence the name) and possess a cubic cleavage. The colour is steel-grey to dark iron-black with bright metallic lustre, but it readily tarnishes, and the mineral soon falls to powder on exposure to the weather. Analysis I (H. Laspeyres, 1876) is of material from Grünau, near Altenkirchen, in Rhenish Prussia, where it occurs intimately mixed with other nickel minerals (gersdorffite, ullmannite, and millerite); deducting 5 p.c. of impurities, this agrees with the formula Ni_4S_5. II (Clarke and Catlett, Amer. J. Sci. 1889, 37, 372) from Sudbury, Ontario, agrees with Ni_3FeS_5. III (D. Browns, Eng. and Min. J. 56, 561) also from Sudbury.

	I.	II.	III.
Ni . .	53·51	41·96	36·85
Co . .	0·61	—	—
Fe . .	3·84	15·57	18·17
Cu . .	—	0·62	4·47
Sb . .	0·51	—	—
As . .	1·04	—	—
S . .	40·27	40·80	38·43
Insol. . .	—	1·02	—
	99·78	99·97	98·45
Sp.gr. . .	4·81	4·54	—

In the Vermilion mine in the Sudbury district the mineral occurs in large amount (some hundreds of tons) intimately intergrown with copper-pyrites and sometimes carrying sperrylite ($PtAs_2$); and it is perhaps present in the nickel ores of some other mines of this district. L. J. S.

POLYGALIC ACID *v.* SENEGA.

POLYGONIN *v.* GLUCOSIDES.

POLYGONUM CUSPIDATUM. *P. cuspidatum* (Sieb. et Zucc.), is common in India, China, and Japan, and is referred to by A. Henry in a paper entitled 'Chinese Names of Plants' (Journal Royal China Branch of Royal Asiatic Society, 22, New Series, No. 5, 1887) as 'Kan-yen, wu-tzu,' the name at Patung for the root of the *P. cuspidatum*, which is said to be used for dyeing yellow.

According to Perkin (Chem. Soc. Trans. 1895, 67, 1084), the main constituent of this root is a glucoside *polygonin* $C_{21}H_{20}O_{10}$, forming orange-yellow needles, m.p. 202°–203°, which, when hydrolysed by acids, gives *emodin* and a sugar

$$C_{21}H_{20}O_{10}+H_2O=C_{15}H_{10}O_5+C_6H_{12}O_6$$

A trace of a second glucoside is also present, from which the *emodin monomethylether*, m.p. 200°, previously found to exist in the root bark of the *Ventilago madraspatana* (Haertn.) (Chem. Soc. Trans. 1894, 65, 932), was obtained. A. G. P.

POLYHALITE. A triple sulphate

$$K_2SO_4\cdot MgSO_4\cdot 2CaSO_4,2H_2O$$

occurring in some abundance in certain salt deposits. In the potash-salt beds of Stassfurt in Prussia and Stebnik in Galicia it is more closely associated with rock-salt, anhydrite, and gypsum; and it is also found with these minerals in the salt mines of Ischl, Ebensee, Aussee, Hallstatt, and Hallein in Austria, Berchtesgaden in Bavaria, Vic in Lorraine, and Varangéville near Nancy. The mineral occurs as nodules with a fibrous or platy structure and a brick-red colour, this colour being due to the enclosure of iron hydroxide. On the artificial production of polyhalite, *v.* J. H. van 't Hoff, Sitz. Akad. Wiss. Berlin, 1906, 412. (*v.* POTASSIUM.) L. J. S.

POLYMERISED OILS *v.* OILS, FIXED, AND FATS.

POLYSTICHIN *v.* FILIX MAS.

POMEGRANATE, *Punica granatum* (Linn.). The fruit is edible. It consists of a hard and thick rind, filled with a pulp containing numerous seeds. König gives, as the composition of the pulp—

Water	Protein	Invert sugar	Cane sugar	Other N-free ext.	Acid	Fibre and seed	Ash
79·3	1·2	11·0	0·7	3·8	0·8	2·8	0·5

Analyses of the juice of pomegranates by Borntträger and Paris (Bied. Zentr. 1899, 28, 198) show that in ripe fruit, the juice contains from 0·37 to 0·51 grm. of acid and from 10·5 to 13·69 grms. of reducing sugar per 100 c.c.; in unripe fruit the free acid amounted to from 3·0 to 3·4 grms., the reducing sugar to from 7·8 to 11·3 grms. The must easily ferments and yields a wine with the flavour of raspberries, containing from 4·4 to 7·0 grms. of alcohol per 100 c.c.

The bark of the stem and roots is used in medicine as an astringent and anthelmintic.

The root bark is the richer in the active principles—the alkaloids—*pelletierine*, iso*pelletierine*, pseudo-*pelletierine* and *methyl-pelletierine*. The first two, constituting usually from 40 to 50 p.c. of the total alkaloids present, are of value as vermifuges: the last two have little or no effect.

The total amount of alkaloids in the bark of the roots grown in the south of France is about 0·6–0·7 p.c., while in the bark of the branches about 0·5 p.c. is present (Ewers, Arch. Pharm. 1899, 237, 49). In the products from Java, the figures were higher (Beckurts, *ibid.* 1900, 288, 8). The alkaloids were first obtained by Tanret (Compt. rend. 1878, 86, 1270) who found pelletierine $C_8H_{15}NO$ to be a colourless liquid, boiling (with decomp.) at 195°, with a sp.gr. of 0·988, soluble in 20 times its vol. of water; its salts are lævorotatory.

iso-Pelletierine is also a liquid of similar composition but is optically inactive; *pseudo*-pelletierine $C_9H_{15}NO$ is a crystalline solid, methyl-pelletierine $C_9H_{17}NO$ is a liquid boiling at 215°, soluble in 25 parts of water and yielding salts which are very deliquescent (*v.* PELLETIERINE).

The alkaloids of pomegranate bark have been studied by Ciamician and Silber (Ber. 1892, 25, 1601; *ibid.* 26, 156; 26, 2738; 1894, 27, 2850); Piccini (Gazz. chim. ital. 1899, i. 408; ii. 311), and Willstätter and Veraguth (Ber. 1905, 38, 1984). The rind of the fruit contains a yellow colouring substance—probably ellagic acid (A. G. Perkin, Chem. Soc. Trans. 1897, 71, 1137). H. I.

POMEGRANATE RIND *v.* TANNINS.

PONCEAU *v.* AZO- COLOURING MATTERS.

PONCEAU CRYSTAL *v.* AZO- COLOURING MATTERS.

POPLAR BUDS. *Chrysin* $C_{15}H_{10}O_4$ is contained in the leaf buds of the poplar (*Populus pyramidalis* (Salisb.), *P. nigra* (Linn.), *P. monilifera* (Ait.)), in which it is present to the extent of about $\frac{1}{4}$ p.c. It was first isolated by Piccard (Ber. 6, 884, 1160; 7, 888; 10, 176) and is best prepared by the method devised by that chemist.

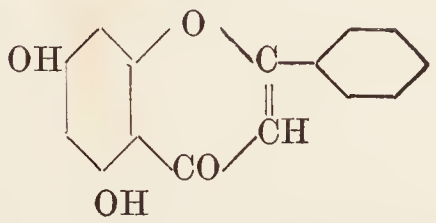
An alcoholic extract of 1000 grams of poplar buds is treated while hot with about 120 grams of lead acetate, and after standing for some time the yellow precipitate is removed. Through the clear filtrate hydrogen sulphide is passed in order to decompose lead salts, the lead sulphide is filtered off and the liquid evaporated to dryness. The residue dissolved in a little hot alcohol gradually deposits crystals of chrysin, which are collected, successively extracted with carbon disulphide, benzene, and boiling water, and finally crystallised two or three times from alcohol.

Pure chrysin crystallises in colourless leaflets, m.p. 275°, and dissolves in alkaline solutions with an intense yellow coloration. When acetylated, *diacetylchrysin* $C_{15}H_8O_4(C_2H_3O)_2$, colourless needles, m.p. 185°, is produced, but by the action of methyl iodide in the usual manner a *monomethylether* $C_{15}H_9O_3{\cdot}OCH_3$, m.p. 163°, can be prepared. The latter yields *acetylchrysinmonomethylether* $C_{15}H_8O_3(OCH_3)C_2H_3O$, colourless needles, m.p. 149°, and with alcoholic soda gives a bright yellow sodium salt which is decomposed by washing with water (*v.* Kostanecki, Ber. 1893, 26, 2901).

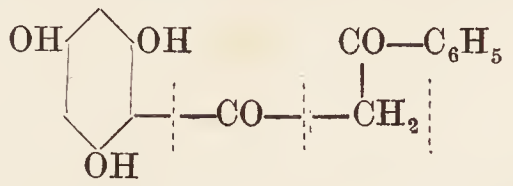
When digested with boiling concentrated potassium hydroxide solution, chrysin gives *phloroglucinol*, *benzoic acid*, *acetic acid* and *acetophenone* (Piccard, *l.c.*), the last-named in very small quantity and the reaction can be expressed as follows:

$$C_{15}H_{10}O_4+3H_2O = C_6H_6O_3+C_6H_5COOH+CH_3{\cdot}COOH$$

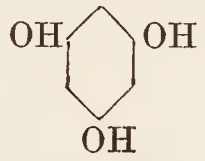
An investigation by v. Kostanecki (*l.c.*) indicates that chrysin is a *dihydroxyflavone* and possesses the constitution



The first hypothetical product of the hydrolysis of chrysin by means of alkali (compare flavone) is 2:4:6-trihydroxybenzoylacetophenone



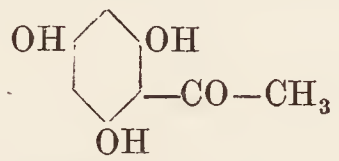
which subsequently yields *phloroglucinol* and *acetophenone* and *carbon dioxide*



$+CO_2+CH_3{\cdot}CO{\cdot}C_6H_5$

Phloroglucinol. Acetophenone.

On the other hand, *phloroacetophenone* (which is unstable in the presence of alkali and is thereby converted into phloroglucinol and acetic acid) and benzoic acid may also be produced.



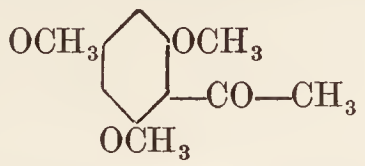
$+C_6H_5—COOH$

Phloracetophenone. Benzoic acid.

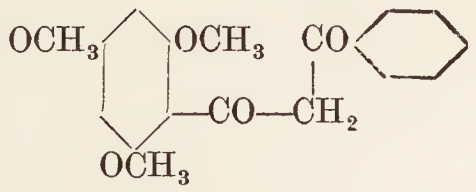
Chrysin has been synthesised by Emilewicz, v. Kostanecki and Tambor (Ber. 32, 2448) in the following manner:

Phloroacetophenonetrimethylether (1) gives, when treated with ethyl benzoate in the presence of sodium, 2:4:6-*trimethoxybenzoylacetophenone* (2).

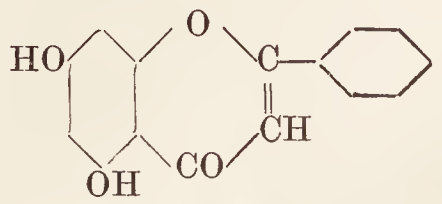
(1)



(2)



(3)



The latter, when digested with strong boiling hydriodic acid, is demethylated and ring formation occurs with the production of chrysin (3).

The following derivatives of chrysin have been prepared :

Dibromchrysin $C_{15}H_8Br_2O_4$ (Piccard, Ber. 1873, 6, 886) ; *Di-iodochrysin* $C_{15}H_8I_2O_4$, yellow needles (Piccard) ; *Dinitrochrysin* $C_{15}H_8(NO_2)_2O_4$, red leaflets, m.p. 272° (Piccard and Darier, Ber. 1894, 27, 21) ; *Chrysinmonoethylether*

$$C_{15}H_9O_3(OC_2H)_5$$

thin needles (m.p. 145°) (Piccard) ; *Chrysin*iso*amylether* $C_{15}H_9O_3(OC_5H_{11})$, thin needles, m.p. 125° (Piccard) ; *Dibromchrysin*iso*amylether*

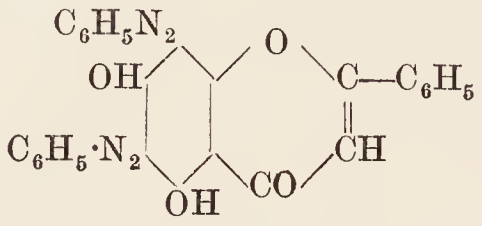
$$C_{15}H_7Br_2O_2(OC_5H_{11})$$

needles, and *dinitro-diacetylchrysin*

$$C_{15}H_6O_4(NO_2)_2(C_2H_3O)_2$$

yellow needles, m.p. 229° (Darier, *l.c.*).

Disazobenzenechrysin (Perkin, Chem. Soc. Trans. 1896, 69, 1439)



orange-red needles, m.p. 251°–252°, insoluble in alkaline solutions, is unaltered by prolonged digestion with acetic anhydride.

Chrysin is a feeble dyestuff. The shades produced on wool mordanted with aluminium, chronium, and iron, are respectively pale bright yellow, pale yellow-orange, and chocolate-brown.

Tectochrysin, a second constituent of poplar buds, is present in the benzene extracts from the crude chrysin. Tectochrysin is chrysin monomethylether ($C_{15}H_9O_3{\cdot}OCH_3$) (Piccard), and is identical with the methylation product of chrysin itself. A. G. P.

POPPY SEED OIL. Poppy seed oil is obtained from the seeds of the two varieties of poppy, *Papaver somniferum* (Linn.), viz. *P. album* and *P. nigrum* (DC.), by pressing. The plant is grown extensively in Asia Minor, Persia, India, Egypt, South Russia, and the North of France. The seeds yield from 45–50 p.c. of oil. The seed produced in Manchuria is grown together with other wild seeds yielding about 16 p.c. of a non-drying oil; hence the Manchurian oil is of very low quality as regards drying powers.

In France a distinction is made between *huile d'œillette* and *huile de pavot*. The former is obtained from indigenous, or at any rate European, grey or blue poppy seed, whilst the name *huile de pavot* is given to the oil obtained from oversea brown or mottled seed. Since by far the greatest part of expressed oils, both of European as also of oversea origin, is used as a table oil, all edible poppy seed oils are termed *huile d'œillette*.

The 'cold drawn' oil, the oil of the first expression, is almost colourless or very pale golden yellow ; this is the 'white poppy seed oil' of commerce. The second quality, expressed at a higher temperature, is much inferior, and constitutes the 'red poppy seed oil' of commerce.

White poppy seed oil forms an emulsion when shaken with air and froths much more persistently than the 'red' oil.

'Sweet' (fine) table oil is prepared by cold expression in Marseilles and in the north of France (in Lille, Arras, Douay, Cambrai). The cold-pressed oil is filtered before being placed on the market. In some of these establishments paper filters are said to be used, even at present.

Poppy seed oil has little or no odour and a pleasant taste, so that it is largely used as salad oil, especially as it does not easily turn rancid. The oil of unsound quality, however, possesses an acrid taste.

The cakes resulting as a by-product are rich in nitrogen and are used as cattle food ; only when the cakes have become mouldy are they employed as a manure for early fruit.

For the chemical and physical characteristics, *see* tables under Oils, Fixed, and Fats.

Poppy seed oil is, as a rule, contaminated with small quantities of sesamé oil, owing to the seed being usually expressed in the same works in which sesamé oil is produced. Edible poppy seed oil is at present frequently adulterated with sesamé oil and also with hazelnut oil to improve the taste of the edible oil obtained from stored seeds.

The differentiation of poppy seed oil from walnut oil is of importance in the examination of white paints. The readiest means for this purpose is furnished by the insoluble bromide test (*see* Oils, Fixed, and Fats). Walnut oil yields from 1·4 to 1·9 p.c. of ether-insoluble brominated glycerides, whereas poppy seed oil yields none.

J. L.

POPULIN (*Benzoyl salicin*) $C_{20}H_{22}O_8{,}2H_2O$ is a glucoside contained in the bark and leaves of the Poplar, *Populus tremula* (Linn.), from which it is extracted by boiling the leaves with water. The extract is precipitated with lead acetate and the filtrate is treated with hydrogen sulphide, after which it is decolorised with charcoal, evaporated and recrystallised (Piccard, Ber. 1873, 6, 890 ; Hallwachs, Annalen, 1857, 101, 372 ; Piria, *ibid.* 1855, 96, 376). It can be readily obtained also by the following process :

A solution of 20 grams of salicin in a litre of water is rendered alkaline with potassium hydroxide and 10 grams benzoyl chloride are added very slowly with constant stirring, more alkali being added from time to time so as to avoid the formation of much free acid. The populin separates as a bulky white precipitate, which is dried, powdered, and extracted with ether. The insoluble residue is recrystallised from boiling water and subsequently from hot alcohol (Dobbin and White, Pharm. J. 1904, 73, 233).

It forms colourless prismatic needles which lose their water of crystallisation at 100°, and melt at 180°. It has a sweetish somewhat acid taste, is lævorotatory (Biot and Pasteur, J. 1852, 179), is sparingly soluble in ether and in cold water but readily so in hot water and in alcohol.

When boiled with lime or baryta water it is decomposed into salicin and benzoic acid. With nitric acid it yields *benzohelicin* $C_{20}H_{20}O_8$, and in strong sulphuric acid it dissolves with a red colour. When boiled with dilute acids it yields *saliretin*, benzoic acid and glycose (Lippmann, Ber. 1879, 12, 1649). *V.* Glucosides.

PORCELAIN *v.* Pottery.

PORCELAIN CLAY *v.* Clay.

PORCELAIN STONE *v.* Clay.

PORCELAINS, DENTAL. Porcelains used

for the production of artificial teeth correspond in composition to the following mixtures :—

	A	B	C	D	E
Felspar . .	81	80	89·5	61·06	12·02
Clay substance .	4	—	—	—	—
Flint . . .	15	—	3·8	29·07	60·49
Quartz . .	—	20	—	—	—
Bone ash . .	—	5	—	—	—
Sodium carbonate	—	—	4·0	1·86	7·90
Calcium ,, .	—	—	2·7	4·21	1·43
Potassium ,, .	—	—	—	1·98	7·21
Borax . .	—	—	—	0·83	10·95

The use of true porcelains for dental inlays has been almost completely replaced by that of porcelain (silicate) cements, which consist of a powder composed of (1) basic calcium and aluminium silicates, with or without gluinum nitrate, (2) zinc oxide, (3) calcined alumina, and a liquid which is a 'modified' solution of phosphoric acid. An analysis of a commercial silicate cement showed the powder to consist of SiO_2 37·0, Al_2O_3 32·2, CaO 7·5, Na_2O 10·1, P_2O_5 1·9, F 9·3, and loss on ignition 2·0 p.c., and the liquid to consist of Na_2O 6·0, P_2O_5 35·5, and water 58·5 p.c.

In making true dental porcelains at York, Pa., the felspar is crushed, hand-picked, then ground in drag mills, 2 ft. 6 in. diameter, and mixed with kaolin, quartz, and a little starch and gum. The mixture is tinted with iron, titanium, cobalt, chromium, copper, manganese, gold, and other oxides. The teeth are made in bronze moulds, paste of the requisite colours being applied to the various parts of the mould. The mould with its contents is heated under pressure so as to bake the mixture lightly. The teeth are then removed, dressed, and burned in a gas-fired muffle on trays made of fused silica. The shortest possible heating is necessary to secure external fusion without warping. The teeth are then annealed in a separate furnace. The metal pins used to attach the teeth to the plate are preferably of platinum and are inserted before burning the teeth. If pins of base metal are used, they are generally soldered to platinum tips in the teeth (A. S. Watts, Trans. Amer. Ceram. Soc. 1915, 17, 190 ; J. Soc. Chem. Ind. 1917, 36, 876).

PORCELAIN (GERMAN), for Chemical and Electrical Ware. The hard paste Berlin porcelain used in the manufacture of evaporating dishes, crucibles, casseroles, tubes, &c., and in the electrical industry for insulators, has a faint greyish-yellow colour which is intensified on heating, but returns to the original tint on cooling. The specific gravity diminishes during burning ; it is 2·64 for unglazed porcelain burned at 950°C., and 2·465 for fully burned ware (1420°C.). The average chemical composition is 67·5 p.c. SiO_2, 26·6 p.c. Al_2O_3, 0·8 p.c. Fe_2O_3, 0·4 p.c. TiO_2, 0·4 p.c. CaO, 0·3 p.c. MgO, 3·3 p.c. K_2O, 0·7 p.c. Na_2O. The crushing strength of 2·5 cm. cubes averages (according to an unpublished communication of Rosenthal) 4200 kilos. per sq. cm. No direct figures for tensile strength and modulus of elasticity are available, but the values are probably similar to those for Hermsdorf porcelain, viz. 1300–2000 kilos. per sq. cm., and 5000–7000 (using the kilo. and sq. mm. as units) respectively. The absolute heat conductivity, or number of calories escaping in one second from a surface of 1 sq. mm. with a temperature-difference of 1°C., is rather greater than that of glass, and may be assumed to be between 0·002 and 0·004. The mean specific heat of unglazed Berlin porcelain (Steger) is 0·202 between 20° and 200°C., and 0·221 between 20° and 400°C. The coefficient of expansion (0·00000336 between 16° and 250°C., and 0·00000434 between 16° and 1000°C., according to Henning, Ann. Chim. 1907, [4] 22, 631) is less than that of ordinary glass, stoneware, and such refractory materials as Marquardt's porcelain and magnesia, and its increase with rise of temperature is also less than in those materials. Hence the Berlin porcelain is able to withstand sudden changes in temperature. Berlin porcelain has no definite melting-point. A rod 80 mm. long and 6 mm. diameter supported at one end was heated over a length of 20 cm. ; it began to bend at 600°C. and was markedly deformed at 900°C., but crucibles and short tubes, &c., if properly supported can be heated up to 1400°C. The melting-point as determined by the Seger cone method corresponds to Seger cone 30–31 (1680°C.). The glaze on the ware begins to soften at 950°C. The porcelain usually contains many minute air-bubbles, but it should be impervious to gases. When a freshly fractured surface is treated with an organic dye, the latter should be entirely removed by washing. One tube tested under a reduced pressure of 30 mm. mercury at 1300°C. was quite impervious to gases, but collapsed suddenly at 1400°C. Pyrometer tubes of Berlin porcelain remain quite impermeable at 1400°C. under ordinary atmospheric pressure. The electrical conductivity at the ordinary temperature is extremely low ; it increases with the temperature, being 300 to 400 times as large at 80°C. The electrical conductivity (reciprocal of the resistance in ohms) of a 1 cm. cube is, according to Dietrich (Zeitsch. physikal. Chem. 1910, 11, 187), $0·25 \times 10^{-12}$ at 97·5°C., and $0·26 \times 10^{-10}$ at 189°C. ; and, according to Goodwin and Mailey (Phys. Rev. 1908, 27, 322), $0·05 \times 10^{-6}$ at 400°C., and 1×10^{-6} at 1000°C. Pirani and Siemens (Zeitsch. Elektrochem. 1907, 13, 969) observed an electrical resistance of $1·7 \times 10^{4}$ ohms per cm. cube at 727°C. or a conductivity of 6×10^{-5} At 300°C. and higher temperatures distinct electrolytic current conduction has been observed (Haber and others, Zeitsch. anorg. Chem., 1908 57, 154). Rosenthal (unpublished communication) found that plates 2·5 mm. thick will withstand a current up to 40,000 volts. The dielectric constant is 5·73 (Starke, Wied. Ann. 1897, 60, 629) as compared with 6·61 to 6·84 for soft felspathic porcelain (Rieke, Zeitsch. angew. Chem. 1915, 28, 374 ; J. Soc. Chem. Ind. 1915, 34, 1093).

True chemical porcelain must withstand rapid changes in temperature ; must be thin, vitreous, and translucent ; the glaze must be so hard that when the ware is heated on a pipe-clay triangle with a blast burner, neither the triangle nor the contents of the vessel adhere to the glaze ; the glaze must resist alkaline solutions ; the ware must not be deformed below a temperature corresponding to Seger cone 25 (1580°). The best body consists of clay 80 p.c., felspar

10 p.c., and quartz 10 p.c. (Montgomery and Babcock, Trans. Amer. Ceram. Soc. 1916, 18, 88). The resistance to fracture in consequence of abrupt changes of temperature requires the bulk of the alumina in porcelain to have crystallised out as sillimanite. The formation of sillimanite is the more complete the lower the proportion of bases present, although a certain proportion of bases is essential to its formation (G. N. White, Trans. Ceram. Soc. 1921–22, 21, 320; Jour. Soc. Chem. Ind. 1923, 97 A).

For an account of English Chemical Porcelain, *see* Watkin (J. Soc. Chem. Ind. 1917, 36, 749).

PORPEZITE. A native alloy of gold and palladium.

PORPHYRITE *v.* PORPHYRY.

PORPHYROXINE. A name first given by Merck in 1837 to a substance prepared from opium, and considered by Hesse to be a mixture of several alkaloids, one of which is meconidine and another probably rhæadine. According to Jitendra Nath Rakshit (Chem. Soc. Trans. 1919, 455) it is a definite substance of the formula $C_{19}H_{23}O_4N$, forming pale yellow or white transparent prisms, m.p. 134°–135°; slightly soluble in water, giving a strongly alkaline solution. Its mineral acid solutions assume on exposure to air a pink porphyry colour; it gives a red colour with strong sulphuric acid, becoming a grass-green on addition of a crystal of potassium dichromate; concentrated hydrochloric acid gives an orange colour, $[\alpha]-139{\cdot}9°$ in chloroform. A number of its salts have been prepared.

PORPHYRY (Fr. *Porphyre*, Ger. *Porphyr*). An igneous rock showing larger crystals of some of the mineral constituents set in a fine-grained ground-mass. Such a structure, known as porphyritic, indicates that there were two distinct periods of crystallisation in the magma. The original porphyry (*πορφυρίτης λίθος, lapis purpureus*) was the famous *porfido rosso antico* [1] quarried by the Romans at Jebel Dokhan in Egypt. This rock shows small white or pink crystals of andesine-felspar set in a base of a rich purple colour, hence the name. According to J. Couyat (who, however, calls the rock a hornblende-andesite), it occurs as the central, more crystalline, portions of volcanic necks of hornblende-porphyrite containing porphyritic crystals of andesine set in a greenish-black or ivory-black ground-mass rich in hornblende and magnetite. By the alteration of this black rock it passes gradually through a violet variety into the red porphyry. The simultaneous decomposition of the hornblende and felspar has given rise to much manganiferous epidote (withamite), but the characteristic red colour is mainly due to the large quantity of finely divided hæmatite derived from the magnetite. On the history of the rock *v.* O. Schneider (Ueber den roten Porphyr der Alten, Dresden, 1887); for a description of the quarries *v.* W. Brindley (Trans. R. Inst. Brit. Architects, 1888); and for petrographical details *v.* J. Couyat (Compt. rend. Paris, 1908, 147, 988).

Another famous antique porphyry is the *porfido verde antico* from Marathonisi in Greece. This shows large white or pale green crystals of labradorite-felspar in a compact dark green base, the green colour being due to secondary chlorite and epidote. This is now known as a diabase-porphyrite, and a rock strikingly similar to it in appearance and characters occurs on Lambay Island, near Dublin.

Although a porphyritic structure is sometimes shown by plutonic rocks, and more often by volcanic rocks, it is more frequently met with in the group of hypabyssal rocks. These occur as dykes and sheets, and have been formed by the intrusion of molten magma along planes of weakness in pre-existing rocks. The conditions under which they consolidated were thus intermediate between those for the deep-seated plutonic rocks and for the surface volcanic rocks. The name porphyry is therefore applied in petrology to this intermediate group of rocks; but usually with the further limitation that porphyry is restricted to the more acid members containing orthoclase (potash-felspar), and the name *porphyrite* used for the more basic containing plagioclase (soda-lime-felspar). The grouping then becomes:

Quartz-porphyry or Granite-porphyry, also called quartz-felsite and elvan, for rocks identical in chemical and mineral composition with the plutonic granites and the volcanic rhyolites, but of intermediate structure.

Orthoclase-porphyry or Syenite-porphyry corresponding with syenite and trachyte.

Hornblende-porphyrite, Mica-porphyrite, or Diorite-porphyrite, corresponding with diorite and andesite.

Labradorite-porphyrite or Diabase-porphyrite, corresponding with gabbro and basalt.

The range in chemical composition of these different types is illustrated by the following analyses: I, Quartz-porphyry (elvan) from Tregoning Hill, Cornwall (J. A. Phillips, 1875). II, Syenite-porphyry from La Sal Mountains, Utah (also ZrO_2 0·04, CO_2 0·13, Cl 0·01, P_2O_5, BaO, Li_2O traces). III, Hornblende-porphyrite, the red partially altered rock (porfido rosso antico), from Jebel Dokhan, Egypt (J. Couyat, 1908). IV, Rhomb-porphyry from Tönsterg, Norway. V, green Labradorite-porphyrite from Murbach, Vosges.

	I	II	III	IV	V
SiO_2 .	72·82	68·96	64·4	58·82	53·29
TiO_2 .	—	0·12	0·65	—	—
Al_2O_3	15·12	15·42	16·1	21·06	18·87
Fe_2O_3	1·75	1·99	3·5	3·26	4·09
FeO .	trace	0·16	1·0	0·70	4·53
MnO .	trace	0·07	trace	—	—
CaO .	0·52	0·25	5·0	3·03	5·71
MgO .	1·06	0·22	2·7	1·38	2·47
K_2O .	6·25	5·48	1·6	3·70	3·66
Na_2O .	0·51	6·59	4·2	6·83	4·07
H_2O .	2·29	0·52	1·1	1·26	2·66
	100·32	99·96	100·25	100·04	99·35
Sp.gr.	2·64	—	—	—	2·76

Porphyries and porphyrites are of wide distribution, and often occur as dykes and offshoots from larger masses of plutonic rocks. For example, in Cornwall and Devon, dykes of quartz-porphyry, locally called elvan, are common in connection with the granite bosses. The elvan of Pentewan, near St. Austell, has been much used for church decoration in the west of England. The mica-porphyrite of

[1] 'Porfido rosso antico' 'and porfido verde antico' are quite distinct from the antique marbles 'rosso antico' and 'verde antico' (*v.* MARBLE).

Canisp, in Sutherland, and the rhomb-porphyries of the Christiania district are very striking rocks, especially when polished. Another porphyritic rock frequently used as a polished ornamental stone is the granite of Shap, in Westmoreland. Other less handsomely marked porphyries are used locally as building stones; and being very hard and tough they are especially suitable for road stones. The diorite-porphyrite of Quenast and Lessines, in Belgium, have been exported to England for this purpose. L. J. S.

PORPOISE OIL. Porpoise oil is obtained from the brown porpoise, *Delphinus phocæna* (Linn.). The oil from the blubber is kept separate from that prepared from the cavities in the head and from the jaw, exactly as in the case of dolphin oil (*see* OILS, FIXED, AND FATS tables). Hence we differentiate between *body oil* and *jaw oil*.

Both oils are characterised by the high proportion of volatile fatty acids they yield on saponification. The jaw oil contains much higher proportions of volatile acids than does the body oil. The oil is used, like dolphin oil, for lubricating delicate machinery, especially type-writing machines. J. L.

PORTLAND CEMENT *v.* CEMENTS.

PORTUGALLO OIL. Essential oil of orange peel (*v.* OILS, ESSENTIAL).

POSIDONIA FIBRE. The fibre of *Posidonia Australis*, a marine plant occurring on the flats on the shores of Western Australia and elsewhere, used as a heat insulator on account of its low conductivity, contains upwards of half its weight of cellulose, and when nitrated, after purification, is capable of yielding a stable gun-cotton (Smart and Pecover, J. Soc. Chem. Ind. 1918, 300 T; *see* also Bulletin 4, South Australia Dept. of Chem., J. Soc. Chem. Ind. 1917, 542).

POTASH-FELSPAR *v.* FELSPAR.

POTASH-MICA *v.* MICA.

POTASSIUM. Symbol K. At.w. 39·1.

Occurrence.—Potassium occurs, principally as chloride and sulphate, in sea-water and other natural waters, a litre of the former containing from 0·5 to 0·7 gram of the element. As chloride or carbonate, or as an organic salt, it occurs in soils and vegetable and animal substances. Thus, wood ashes contain much potassium carbonate, which also forms a considerable proportion of the ash of marine plants, such as *laminaria* and *fuci*. Potassium occurs as *sylvine* or *sylvite* KCl, and as *carnallite* $KCl{\cdot}MgCl_2{,}6H_2O$, in the beds overlaying the salt deposits of Stassfurt. Similar deposits occur in Alsace, Spain, Galicia, Abyssinia, California, and elsewhere. As nitrate, it is found as an efflorescence on the soil, usually together with the sodium salt, in Peru, Chile, &c., and as an important constituent of many mineral waters, such as those of Harrogate and Vichy. As the double sulphate of aluminium and potassium, it occurs in *alumstone* or *alunite* $3Al_2SO_6{\cdot}K_2SO_4{,}6H_2O$, principally in trachyte and other rocks subjected to the action of sulphurous gases. It is found as bitartrate in wines, and as sulphate, carbonate, and chloride in beetroot molasses. As an organic salt (sudorate), it occurs in the 'suint' of sheep, and is separated therefrom as carbonate together with wool fat (Langbeck, J. Soc. Chem. Ind. 1890, 356).

The main sources of naturally occurring potassium compounds are the primitive rocks, in which it occurs as *orthoclase* (potash felspar) $Al_2O_3{\cdot}K_2O{\cdot}6SiO_2$; *muscovite* (potash mica) $K_2O{\cdot}3Al_2O_3{\cdot}4SiO_2$, *leucite* $K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$; *apophyllite* $4(CaO{\cdot}2SiO_2{\cdot}H_2O)KF$, and other zeolites, and in many other silicates.

The sources from which potassium salts are obtained for technical purposes are—firstly, sea-water; secondly, the mineral crust of the earth; thirdly, the vegetable, and to some extent the animal, kingdom.

The quantity of potassium salts contained in *sea-water* is not very large, but it has been found economically possible to extract it in the form of potassium chloride. Indirectly, the potassium salts obtained in the working up of kelp are derived from this source.

The *mineral crust of the earth* contains about 2·4 p.c. K_2O in the state of *silicates*, as a constituent of several important minerals as felspar and mica; hence both older and younger rocks (granite, mica, slate, basalt, &c.) are sources of potash. By the decay of the rocks containing these minerals, potassium compounds have been spread all over the earth as part of the arable soil; from this source are derived, not only the potassium compounds contained in all plants, but probably most of those contained in sea-water. The importance of this occurrence of potash is enormous for the existence of all organisms; but it has not been economically possible to extract potassium compounds for technical purposes from the natural silicates or the arable soil.

Several other naturally occurring salts of potassium are, however, better adapted for this purpose. Potassium *nitrate*, as found in the crude state, especially in India, is certainly more valuable in respect of its acid than of its alkaline constituent; but the latter is also important, as is proved by the large quantity of potassium chloride employed for the manufacture of artificial saltpetre.

Potassium sulphate occurs in large quantities in alum rock, and in several of the minerals found together with carnallite in the Stassfurt and other deposits.

Potassium chloride is found both in the pure state, as *sylvine*, and in much larger quantities as *carnallite*, in the Stassfurt deposits and elsewhere. This is at present the most important of all the sources from which potassium salts are obtained for technical purposes.

In the *vegetable kingdom* potassium is found principally in the liquid contents of the cells and vessels, chiefly combined with organic acids. On burning it appears in the ashes as carbonate, together with more or less sulphate, chloride, phosphate, and silicate. These potassium compounds are, of course, derived from the soil on which the plants grow; but for many centuries, indeed, apart from saltpetre and kelp, nearly up to the middle of the nineteenth century, *wood ashes* formed practically the only source of potassium compounds employed for technical purposes. Another important source of potassium salts is the ashes of *seaweeds*, called *kelp* in Scotland and *varec* in Normandy, which from times immemorial have been obtained by employing the seaweed as fuel; since 1811, when iodine was discovered in these ashes, and a special industry had been founded thereon, those potassium salts have also been utilised.

The Pacific kelps are exceptionally rich in potash salts, and it is stated that even on a moderate estimate it should be possible to obtain annually at least a million tons of potassium chloride from this source. Attempts were made in the United States during the Great War to extract potash from seaweed on a commercial scale (*v. infra*) (J. Soc. Chem. Ind. 1912, 31, 1177). For the potash content of the giant kelps of the Alaskan coast, *see* Merz (J. Soc. Chem. Ind. 1914, 6, 19). The available beds of the Pacific coast and the annual harvest of kelp, with the resultant quantities of potassium chloride, have been estimated as follows :—

Region	Area sq. m.	Fresh kelp (tons)	KCl (tons)
Cedros Island to San Diego . . .	91·4	16,979,800	649,000
San Diego to Point Conception . .	97·9	18,195,300	696,000
Point Conception to Cape Flattery .	36·2	4,377,400	167,000
Puget Sound . .	5·0	520,000	20,000
South-East Alaska .	141·6	15,666,000	598,000
Western Alaska .	17·9	3,367,000	136,000
Total . .	390·0	59,105,500	2,266,000

The principal kelps available are *Macrocystis pyrifera*, *Nercocystis luetkeana*, and *Alaria fistulosa*, in which the amount of potash (K_2O) varies from 9·1 p.c. to 20·1 p.c. (Cameron, U.S. Commerce Rept. No. 143, 1915).

Somewhat later another vegetable source was opened out for potassium compounds—viz. the *vinasse*—that is, the residue left on distilling fermented beet-root molasses. Hence the expression 'vegetable alkali,' by which potash was distinguished from soda, when Duhamel, in 1736, had proved the separate existence of those bodies, was altogether appropriate, not only at this time, but even much later, until the Stassfurt discoveries made that designation altogether unsuitable.

Even the animal kingdom contributes a certain quantity of potassium compounds, in the shape of the carbonate of potash from the 'yolk' of *sheep's wool* (*suint*).

Interesting communications on the history of potashes are made by E. O. von Lippmann in Chem. Zeit. 1908, 977.

Metallic potassium. The compound nature of the alkalis, and the presence in them of oxygen, had been suspected previous to 1807 (*v.* Lavoisier, Traité de Chimie, II. 194), but the isolation of potassium was not effected until that year, when Davy obtained it by electrolysis of the fused hydroxide (Phil. Trans. 1808, 1 ; 1809, 39 ; and 1810, 16). The metal was soon prepared in larger quantity by Gay-Lussac and Thénard (Ann. Chim. 1808, 65, 325, and 1808, 66, 205) by slowly passing the hydroxide over iron filings heated to whiteness in a gun-barrel protected by a luting of clay, their process being modified by Berzelius (Gilbert's Annalen, 6, (N. F.) 198), Mantell (Annals of Philosophy, Thompson and Phillips, 22, 232), Gmelin (Handb. 3, 5), and Tennant (Annalen, 93, 291).

An important improvement was next introduced by Curandau (Ann. Chim. 1808, 66, 97, and Phil. Mag. 1810, 36, 283), who replaced the iron by carbon or carbonaceous matter. This, and the other processes in use, were examined by Brunner (Bibliothèque Universelle de Genève, 1823, 22, 36, and Schweigger's J. für Chem. und Phys. 35, 517), who also improved upon the apparatus employed by Bucholz (Ann. Chim. 73, 78), Trommsdorff (Gilbert's Annalen, 30, 333), Lampadius (Schweigger's J. für Chem. und Phys. 34, 221), and others.

Brunner's process as improved by Wöhler (Pogg. Ann. 1825, 4, 23, and 474), consists in carbonising potassium bitartrate in a covered vessel, and heating the resultant mixture of carbon and potassium carbonate with powdered charcoal in a mercury bottle, at the temperature of a powerful wind furnace. Kukla (Zeitsch. für Phys. und verwandte Wissenschaften, 1837, 5, 466), Werner (J. pr. Chem. 14, 267), Schœdler (Annalen, 20, 2), and Gale (Amer. J. Sci. 19, 205, and 21, 60), proposed various arrangements and lutes for protecting the retort from the furnace, the two first, and Pleischl (Zeitsch. für Phys. und verwandte Wissenschaften, 2, 307, and 343, 3, 326) also proposing modifications in the mixture used.

The method of condensing was next improved by Donny and Mareska (Ann. Chim. [iii.] 35, 147, *v.* also Mitscherlich, Lehrb. der Chem. 2, 10) ; while the addition of chalk to the mixture was found to facilitate the reduction by rendering the mass pasty instead of liquid at the reduction temperature, thus preventing the separation of the carbon from the alkali (*v.* Deville, De l'Aluminium (Paris, 1859), 650 ; and Kühnemann, J. 1864, 180).

For the preparation of potassium in a state of greater purity, Matthiessen (Chem. Soc. Trans. 1855, 8, 27) proposed the electrolysis of the easily fusible mixture of potassium and calcium chlorides.

The use of sodium instead of potassium for the manufacture of aluminium was introduced in 1854 by Deville (Ann. Chim. 1856, 46, 514), who also made improvements in the manufacture of the metal. Since then, sodium has almost entirely replaced potassium for use in the arts. The inconvenience and waste attending the manufacture of potassium, owing to the production of explosive compounds with carbon monoxide (*v.* Liebig, Annalen, 11, 182, and Brodie, Chem. Soc. Trans. 12, 269), accounted to some extent for its former high price. By Castner's electrolytic process potassium can be produced at a price not greatly exceeding that of sodium.

Potassium may also be made by melting together metallic sodium and potassium hydroxide out of contact with air, when sodium oxide is formed and potassium and hydrogen are volatilised (Loebel, D.R.P. 307175).

Various processes employed in the preparation of potassium are identical with those used in sodium manufacture, and are described, together with a list of patents and other matters relating equally to both metals, in the article Sodium.

Potassium obtained by any process in which carbon monoxide is a constituent of the evolved gases, always contains the explosive compound above mentioned, which renders it liable to detonate on the slightest friction. For this reason, it must be redistilled, once or twice, when so prepared.

Properties.—Potassium, when freshly cut, has a brilliant, silvery metallic lustre. It crystallises

in obtuse octahedra, showing a greenish-blue tint (Long, Chem. Soc. Trans. 1860, 13, 124).

According to Baumhauer (Ber. 6, 655), its sp.gr. at 13° is 0·875 (0·859, Hackshill, Compt. rend. 1911, 152, 259). At 0°, potassium is brittle, and possesses a crystalline fracture: its coefficient of expansion between 0° and 58° is 0·00025, when liquid 0·00028 between 70° and 100°. At 15°, it acquires a waxy consistency and a few degrees higher becomes pasty, melting at 62·5° (Bunsen, J. 16, 178) and boiling at 762·2° under a pressure of 760 mm. (Heycock and Lamplough). The vapour has a green colour, and attacks glass and porcelain. Its characteristic channelled absorption spectrum has been examined by Roscoe and Schuster (Proc. Roy. Soc. 22, 362). *See* also Datta, *ibid.* 1922, 101, 530. According to Aston, potassium is a mixture of two isotopes of masses 39 and 41.

The lowering of the melting-point of potassium by the presence of sodium, gold, and thallium has been studied by Heycock and Neville (Chem. Soc. Trans. 1889, 666).

Potassium dissolves in liquefied anhydrous ammonia forming a deep-blue solution, from which the metal is re-obtained on evaporation of the ammonia (Seeley, Chem. News. 23, 169). It is the most electro-positive element known with the exceptions of cæsium and rubidium, and is an extremely powerful reducing agent. Hence the use of potassium for the preparation of less electro-positive elements, such as boron, silicon, magnesium, aluminium, &c., for the reduction of gases containing oxygen out of organic and other compounds.

On exposure to the air, it rapidly becomes converted into the hydroxide and finally into the carbonate. It decomposes water at −105° and at higher temperatures with sufficient energy to ignite the liberated hydrogen. Carbon dioxide passed over heated potassium is reduced to carbon, with formation of potassium oxide.

Potassium unites directly with the halogens and with sulphur, selenium, tellurium, and phosphorus, burning brilliantly when heated with them. When heated in carbon monoxide it forms a black mass identical with the explosive body produced in the manufacture of potassium. It may be distilled unaltered in perfectly dry oxygen. For the absorption spectrum of its vapour, *see* Snehamoy Datta, Proc. Roy. Soc. 1922, A, 101, 539.

Alloys.—Potassium forms alloys with most metals, usually by being heated with them. The more important alloys are described under the various metals. With *sodium*, potassium forms alloys of low melting-point, as observed by Davy. Greville Williams (Chem. News. 3, 21) obtained an alloy melting below the ordinary temperature and containing about one-fourth its weight of potassium by heating sodium with potassium hydroxide to about 171°; whilst Wanklyn (Chem. News. 3, 66) obtained a similar alloy by heating sodium with potassium acetate.

Potassium combines directly with *mercury*, with evolution of heat. The melting-points of a number of these amalgams have been determined by Merz and Weith (Ber. 14, 1445). When containing 70–96 parts of mercury to 1 part of potassium, the amalgam is crystalline. With 30 parts of mercury, it is hard and brittle. When heated to 440°, they all leave a crystalline amalgam of the composition HgK_2, spontaneously inflammable on exposure to air (De Souza, Ber. 9, 1050), but all the mercury is evolved below a red heat. Kraut and Popp (Annalen, 159, 188) have prepared a crystalline amalgam of the composition $Hg_{24}K_2$.

Potassium hydride is prepared by passing hydrogen into the metal at 350° (*cf.* Ephraim and Michel, Helv. Chim. Acta, 1921, 4, 762).

Potassium oxide, K_2O, is formed by the slow oxidation of the metal and may be made (D. R. P. 143216) by heating potassium nitrate with metallic potassium, air being excluded: $KNO_3+5K=3K_2O+N$. For the same purpose the nitrite KNO_2 may be employed, and in the same manner mixtures of K_2O and Na_2O may be obtained.

Potassium peroxide, K_2O_4, is a bright orange-yellow substance formed by the ultimate oxidation of potassium, and was industrially prepared by Jaubert (D. R. P. 189822) by heating, with special precautions, an alloy of potassium with lead, tin, or sodium at a moderate temperature in a current of air.

Potassium hydroxide *v. infra.*

Potassium chloride. This salt, which in commerce is generally known as '*muriate of potash*,' was formerly obtained as a by-product in working up kelp for iodine, from the spent lye of soapmakers, in refining native saltpetre, &c. The quantities thus obtained were not very large, and were principally used in the manufacture of alum and of potassium chlorate. Potassium chloride was afterwards obtained in Balard's process of working-up the mother-liquors from the manufacture of sea-salt, and still more in the manufacture of potashes from vinasse (*cf. Potassium carbonate, infra*).

But the quantities thus obtained were insignificant compared with that procured from the *Stassfurt carnallite* and from the Alsatian deposits. We shall first describe the Stassfurt occurrence of potassium salts, as well as the methods of manufacture pursued there.

The village of Stassfurt is situated on the river Bode, not far from Magdeburg, in Prussian Saxony, close to the borders of the small principality of Anhalt. The Stassfurt brine-springs are mentioned as far back as 1227, and in the last century 7000 tons of salt per annum were made there in 30 salt-pans; but about 1815 the production of salt from brine was stopped there, having ceased to be remunerative in the face of competing brine-springs. In 1839 the Prussian mining office commenced boring for rock-salt, and in 1843 the salt was struck at a depth of 850 feet. The boring was continued for another 1080 feet without getting to the bottom of the stratum of salt; but the brine pumped up was extremely impure, containing, together with sodium chloride, a large quantity of magnesium chloride, potassium chloride, and magnesium sulphate. It was conjectured that these salts might be deposited in separate strata, and it was resolved to sink two shafts. These were commenced in 1852, and within five years they had reached a thick stratum of pure rock-salt, after having penetrated a number of strata of other salts, of an aggregate thickness of 530 feet, which were called 'abraumsalze,' because they were at first considered useless, and had to be taken away before getting to the rock salt.

Later on it was found that the salt deposits occupy an enormous basin in the North German Plain, which has been successfully tapped in several other places, of which we mention only Sperenberg, near Berlin, where the boring was continued through the enormous thickness of 3940 feet of salt without getting to the bottom; also at Segeberg, near Lübeck, and in other places. The German mines with their 1500 sq. km. and 200 pits could supply the requirements of the world for 7500 years at the pre-war rate of consumption. Large deposits of sylvine are found in Upper Alsace, in an area of about 180 square kilos., near Mülhausen. Two strata have been found, the upper one 3 feet thick, the lower one more than 16 feet thick, estimated to contain some 1500 tons, but the borings are deep, say 1600 to 2100 feet, which entails a very high temperature. This field, unlike the North German deposits, seems to be continuous, without faults. Geologically it is much more recent than the Stassfurt beds. A full description of these deposits by Paul Kestner is given in the J. Soc. Chem. Ind. Nov. 15th, 1918. According to Matignon these deposits could supply the world's requirements for 300 years at the pre-war rate of consumption.

The profiles (Figs. 1 and 2) give an idea of the strata pierced in the two oldest and most important shafts at Stassfurt and Leopoldshall.

At Stassfurt itself the total thickness of the salt strata is estimated at about 2500 feet, and the time necessary for their formation at about 8000 years. F. Bischof, who has examined them most thoroughly, divides them into the four following 'regions,' of which only the first and the last have become of technical importance.

1. *Anhydrite or rock-salt region,* so called

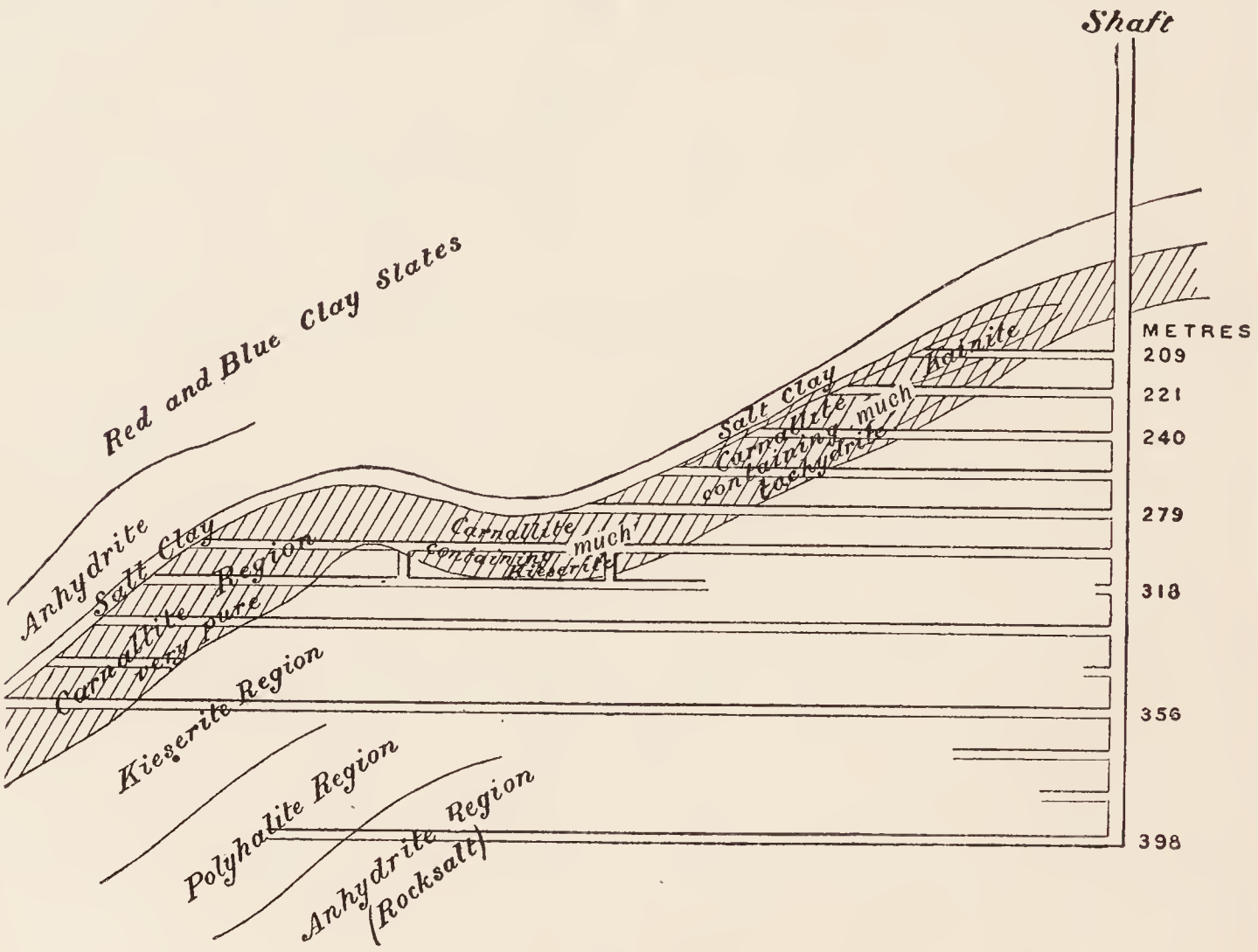


FIG. 1.

from the strings of anhydrous calcium sulphate which divide the rock-salt into bands of an average thickness of nearly 4 inches, each of which is supposed to be a year's growth. The layers of calcium sulphate are only $\frac{1}{4}$ inch thick, and amount only to 4 p.c. by weight of the rock-salt in the upper strata, or 9 p.c. in the lower strata. By mechanically separating the anhydrite, rock-salt of 99 p.c. NaCl can be obtained on a large scale. Small quantities of *hydroboracite* ($CaMgB_6O_{11},6H_2O$) and of a strontium sulphate are found here as well. The thickness of this stratum varies a great deal; in the centre of the basin it is estimated at about 2000 feet.

2. *Polyhalite region.*—Here the rock-salt is already mixed with mother-liquor salts, of which the dominant one is *polyhalite*

$$2CaSO_4,MgSO_4,K_2SO_4,2H_2O$$

Magnesium chloride accompanies the rock-salt, and small quantities of sulphur and of bituminous substances are found here. The average composition of this stratum is: 91 rock-salt, $6\frac{2}{3}$ polyhalite, $\frac{2}{3}$ anhydrite, $1\frac{1}{2}$ magnesium chloride; its thickness is 207 feet.

3. *Kieserite region,* so called from the occurrence of white bands of kieserite $MgSO_4,H_2O$. The average mixture is:

65 p.c. rock-salt
17 „ kieserite
13 „ carnallite
3 „ bischofite, $MgCl_2,6H_2O$
2 „ anhydrite.

This stratum has a thickness of 187 feet.

4. *Carnallite region.*—This contains 55 p.c. of *carnallite* $KCl,MgCl_2,6H_2O$, the most valuable of the Stassfurt salts, together with 25 p.c. rock-salt, 16 p.c. kieserite, the remaining 4 p.c. consisting of magnesium chloride (*bischofite*) $MgCl_2,6H_2O$, magnesium bromide $MgBr_2,6H_2O$, *tachydrite* ($CaCl_2,2MgCl_2,12H_2O$), *boracite* or *stassfurtite* ($2Mg_3B_8O_{15}$), *anhydrite* $CaSO_4$,

reichhardtite ($MgSO_4,7H_2O$), clay, sand, micaceous oxide of iron, &c. The thickness of this stratum is 140 feet.

In some places the action of water has produced important changes in this region which have replaced the kieserite and part of the carnallite by *kainite* $K_2SO_4,MgSO_4,MgCl_2,6H_2O$; or $KCl,MgSO_4,3H_2O$, according to another way of grouping the constituents (about 55 p.c. of the whole), part of which has passed over into *schoenite* (*picromerite*) $K_2SO_4,MgSO_4,6H_2O$. In other places the magnesium chloride has been washed out entirely, and the mixture contains 20 p.c. of pure potassium chloride, *sylvine*, with 30 to 40 p.c. of rock-salt, and an equal quantity of kieserite and other impurities. Only exceptionally *astrakanite* $Na_2SO_4,MgSO_4,4H_2O$ is found.

Other Stassfurt minerals of minor importance are: *leonite* $K_2Mg(SO_4)_2,4H_2O$;

löweite $K_2Mg(SO_4)_2,2\frac{1}{2}H_2O$

langbeinite $K_2Mg_2(SO_4)_3$; *glaserite* $K_3Na(SO_4)_2$; *vanthoffite* $Na_6Mg(SO_4)_4$;

krugite $K_2MgCa_4(SO_4)_3,2H_2O$

pinnoite $MgB_2O_4,3H_2O$;

ascharite $Mg_6B_6O_{15},2H_2O$

kaliborite or *heinzite* $KMg_2B_{11}O_{19},9H_2O$; *magnesium sulphoborite* $3MgSO_4,2Mg_3B_4O_4,12H_2O$.

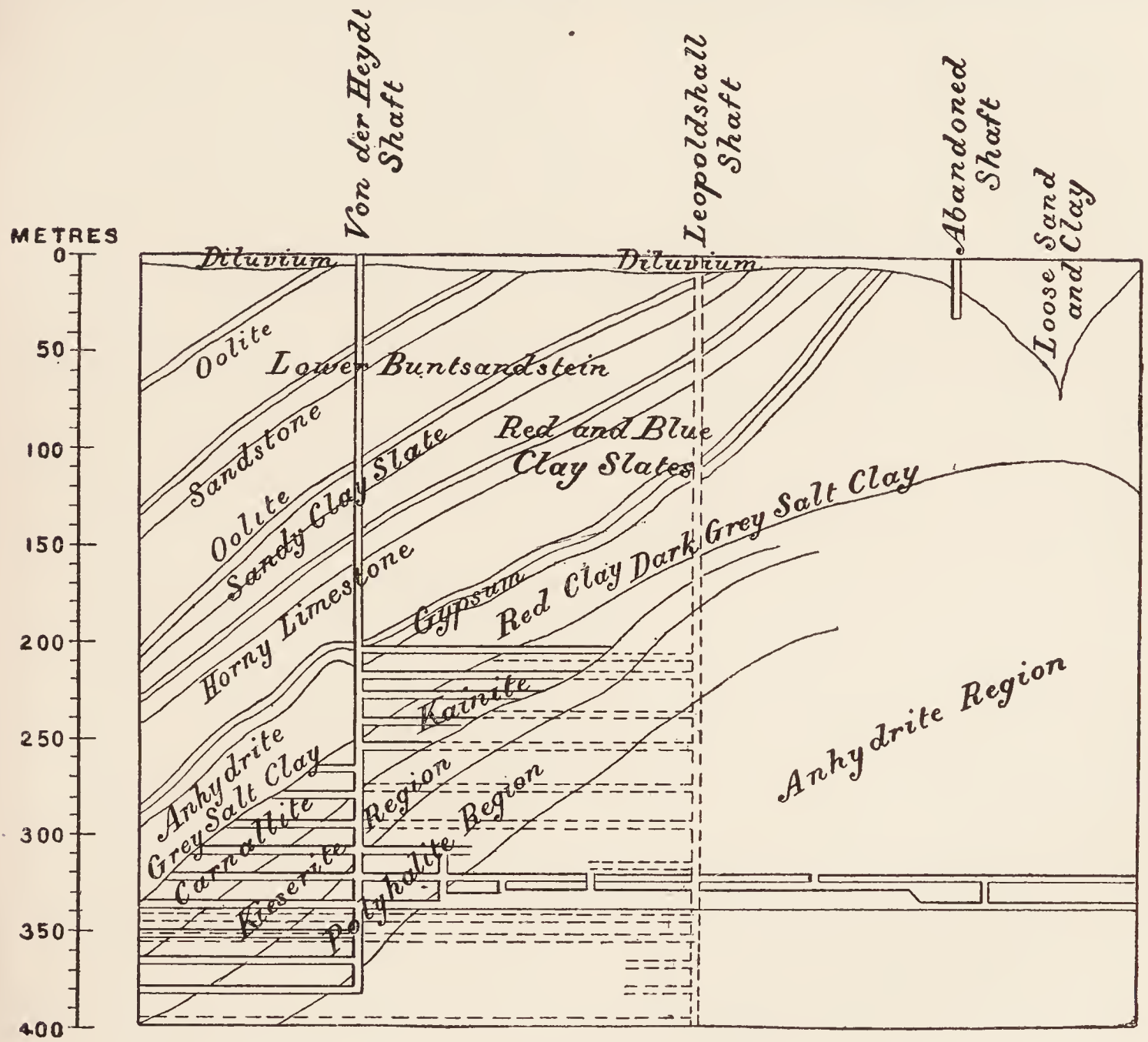


FIG. 2.

The salts are covered by from 20 to 33 feet of *salt clay*, over this from 133 to 300 feet of *anhydrite*, and this again by 80 to 100 feet of very pure, transparent *rock-salt*, free from calcium sulphate, evidently a secondary formation.

Formation of the Stassfurt deposits.—There can be no doubt that the formation of the salt deposits of the North German Plain has been caused by the evaporation of sea-water. But there must have been special causes why, in a comparatively small part of that large area—viz. in the vicinity of Stassfurt—potassium and magnesium salts have been separated in large quantities, whilst on the greatest part of the ground only rock-salt and anhydrite are found.

According to Regnault, the average composition of sea-water is:

Total percentage of solids .	3·53
consisting of:	
Sodium chloride . . .	76·49
Potassium chloride . .	1·98
Magnesium chloride . .	10·20
Magnesium bromide . .	0·06
Magnesium sulphate . .	6·51
Calcium sulphate . .	3·97
Calcium bicarbonate . .	0·08
	99·29

We find here all the materials for the formation of the Stassfurt deposits, the average

composition of which has been stated by Bischof, as follows:

	Percentage expressed in minerals
Rock-salt	85·1
Anhydrite	3·7
Polyhalite	0·8
Kieserite	3·3
Carnallite	6·2
Magnesium chloride	0·9
	Percentage expressed in salts
Sodium chloride	85·1
Potassium chloride	1·7
Potassium sulphate	0·2
Magnesium chloride	2·6
Magnesium sulphate	3·1
Calcium sulphate	4·0
Chemically-combined water	3·3

Since Bischof's time the bottom of the deposit has been reached, and it can now be said that the percentage of sodium chloride and of calcium sulphate is much higher than he assumed.

If we compare the composition of the Stassfurt deposits with the results of the artificial evaporation of sea-water as carried out in 1849 by Usiglio (Ann. Chim. [iii.] 27, 92), we find that there are some differences, partly caused by the long duration of the natural process and its yearly interruption, partly by the loss of mother-liquor (*v. infra*). The various salts were transformed into the minerals now present by a subsequent loss of water and by their mutual interaction, and a regular succession of those minerals was formed through long periods, caused by the autumnal influx of fresh sea-water. One remarkable difference also is this: whilst in artificial evaporation the calcium sulphate is entirely precipitated at an early stage, it is formed at Stassfurt even in the strata consisting of mother-liquor salts. Why the calcium sulphate at Stassfurt is in the form of anhydrite, not in that of gypsum ($CaSO_4,2H_2O$), as in the artificial evaporation of sea-water, we understand now from the observations of Hoppe-Seyler (Chem. Zentr. 1866, 217) and Rose (*ibid.* 1871, 613), according to which the hydration water of gypsum is abstracted from it by contact with a *nearly-saturated* solution of sodium chloride, a condition which we must assume to have existed at Stassfurt.

It is quite evident that the Stassfurt deposits have not been formed by the simple evaporation of a basin of normal sea-water, which would have been required to possess a depth of about 30 miles, and which would have produced a very different arrangement of salts. There must have been conditions similar to those even now found present in some of the Sarmatian lakes. Thus Göbel found at the bottom of Lake Elton a salt deposit of a thickness of 12 feet, consisting of 100 annual layers, which increased in strength and hardness from the top downwards, and at the bottom were as hard as stone. This lake is filled with a saturated brine; by the surface-evaporation in summer, crusts of common salt are formed, which sink to the bottom. Later on, the common salt gets mixed with Epsom salt and other mother-liquor salts, which form a porous, bitter, and deliquescent layer. The autumnal rains and floods partly dissolve and partly condense this top layer, and at the same time cover it with black mud, thus forming a distinct boundary line upon which the next year's crusts are formed again. In spring the water of that lake contains 13·5 p.c. sodium chloride and 10·5 p.c. of magnesium chloride; in autumn it holds but a small quantity of liquor containing only 4 p.c. NaCl, with 20 p.c. $MgCl_2$.

The nearest approach to the Stassfurt conditions is found in the Adji-Darja Bay, in the east of the Caspian Sea, a bay of a superficial area of 2000 or 3000 sea miles, and almost entirely separated from the Caspian by a bar. There is, however, a small channel through which the water, abstracted by the intense evaporation within the bay, is replenished from the Caspian. This causes a continuous separation of salt, which is estimated by Schleiden at about 400,000 tons per diem, and the formation of a mother-liquor, part of which finds its way back into the Caspian. Where the depth of the bay is greater, the concentrated liquor sinks to the bottom, causing a state of sursaturation at this place and the deposition of mother-liquor salts. Without this, practically all the mother-liquor would flow back over the bar, and no mother-liquor salts would be formed; and this seems to have been the condition of most of the rock-salt, forming basins of former geological periods. In the case of the Stassfurt salts we must undoubtedly assume an *intermittent* influx of water, and also a number of geological elevations and depressions of level in order to account for the succession of the various strata. We may, with very great probability, assume the following play of causes: the Stassfurt basin was a valley, inclosed by two longitudinal folds of the earth's crust, communicating at one end with the ocean by a shallow bar, over which, in autumn, the gales and high tides carried large quantities of sea-water; not sufficient, however, to replace the water lost by evaporation. For a long period only gypsum was deposited here; afterwards common salt was formed as well, which converted the gypsum into anhydrite, but which for a long time was re-dissolved every autumn by the dilution of the liquor, caused by rain and floods. Thus the thick crust of gypsum and anhydrite was formed which lines the bottom of the basin. Later on, the liquor became more and more concentrated; the crusts of common salt now became permanent, and the yearly deposits increased in thickness. The sursaturation of the liquor at the bottom caused the transformation of the common salt into rock salt (as first proved by Mohr). Just as we observe it now in the 'salt gardens' on the Mediterranean, the last portions of the summer salt contained a little gypsum, but the greatest quantity of gypsum was precipitated when the strong brine came into contact with fresh sea-water breaking over the bar, thus forming a distinct line of separation against the next year's deposits in the shape of the 'anhydrite strings.' Since there was less and less room in the basin for fresh sea-water, those strings decreased in thickness during this period, which must have lasted several thousands of years, during the later part of which the yearly deposits had an average thickness of $3\frac{1}{2}$ inches. Owing to further concentration of the liquor the crusts of salt in the later part of summer were more

and more mixed with Epsom salt, which appears also with the gypsum precipitated soon after by the influx of fresh sea-water. In this period, which must have lasted 500 or 600 years, *polyhalite*, $K_2SO_4,MgSO_4,2CaSO_4,2H_2O$, was formed in the following way: some carnallite, $KCl,MgCl_2,6H_2O$, formed in summer, was at that period always decomposed in autumn by fresh sea-water, and the potassium chloride thus set free and coming into contact with the deposited Epsom salt was converted into potassium sulphate, which met with enough magnesium and calcium sulphates to form polyhalite. Exceptionally, indeed, carnallite is actually found in that region. During the next period of 500 years, with increasing concentration, some carnallite was regularly formed, but the principal deposit at that time consisted of *kieserite* $MgSO_4,H_2O$. It has been proved by Precht (Ber. 14, 2131) that from a concentrated solution of magnesium chloride, such as must have filled the basin at that period, the magnesium sulphate is separated by evaporation, not in the state of Epsom salts ($MgSO_4,7H_2O$), but in that of kieserite. This compound being insoluble, as well as the anhydrite, the formation of polyhalite was not any more possible.

During the fourth and last period of 500 years, when there was less room for the influx of fresh sea-water, the formation of *carnallite* got the upper hand. Pfeiffer has proved that that salt, and even hydrated magnesium chloride, can be made to crystallise by spontaneous evaporation at the temperature of hot summer days in our present climate. The formation of carnallite must have been still abundant, and a deep layer of mother-liquor, in which magnesium chloride prevailed, must have been standing over the potash-bearing strata when new geological changes caused the eruption of a mighty mass of clayey mud, charged with organic substances, which sank to the ground, forming a layer of salt clay, 26 feet thick, which protected the underlying strata against a subsequent solution of the salts previously deposited, even after the mother-liquor had run off. The loss of that liquor accounts for the difference between the average composition of the Stassfurt deposits and that of the sea-water (comp. above). Wherever such accidental protection was not afforded, the surface-water must have redissolved the upper strata, which accounts for the general absence of mother-liquor salts in other localities.

Apart from Stassfurt and Alsace, the following occurrences of potassium salts require mentioning:—

In 1866 at Kalusz, in Eastern Galicia, potassium salts were found in large quantities, principally consisting of sylvine and kainite, and a large manufacturing industry was commenced. But the quality of the salt proved inferior to the first samples, and in 1875 the works were discontinued, for various reasons, as being unable to compete with Stassfurt.

Considerable deposits of carnallite and sylvine are known to occur at Suria and elsewhere in Catalonia, but owing to political troubles in Spain no effective steps have apparently been taken to work them by the Solvay Company and the two or three Spanish syndicates to whom concessions have been granted.

Large deposits of potassium salts also occur at Erythrea, and have been worked by Italians. They appear to be of more recent formation than the European deposits.

Small quantities of potassium salts, always of poor quality, have been found in the Punjab, in Persia, and in Colorado. None of these deposits gives any promise of industrial application.

The *rock-salt* in the mines round Stassfurt is not now obtained from the lower strata, where the admixture of anhydrite brings it down to 95 p.c., but from the upper (secondary) strata at Neu-Stassfurt, where it comes up to 99 p.c. of real sodium chloride. There is also a large quantity of pan-salt made in the neighbouring Schönebeck salt works.

The average composition of *crude carnallite* is

	Per cent.
Potassium chloride	15·7
Sodium chloride	21·5
Magnesium chloride (with a little bromide)	21·3
Calcium chloride	0·3
Magnesium sulphate	13·0
Insoluble (anhydrite, clay, &c.)	2·0
Water	26·2

Small quantities of rubidium (0·001–0·003 molecules), cæsium and ammonium, and of bromine (0·005–0·01 mol.) are always present in carnallite.

Crude kainite generally contains:

	Per cent.
Potassium sulphate	24·0
Magnesium sulphate	15·5
Magnesium chloride	13·0
Sodium chloride	31·0
Gypsum and clay	1·5
Water	14·0

Hartsalz is a mixture of about 20 p.c. sylvine, 25 p.c. kieserite, and 55 p.c. rock-salt.

Sylvinite is the name given to crude kainite or hartsalz, if the percentage of potassium exceeds 13 p.c. K_2O.

Crude sylvine (not to be confounded with sylvinite) is a raw material of great importance, consisting of varying quantities of sylvine and rock-salt; the percentage of KCl varies from 25 to 50, sometimes even 80 or 90 p.c.

Crude kieserite is very impure, much more so than the residual product obtained in the manufacture of potassium chloride.

Boracite, with 52 or 53 p.c. crystallised boracic acid, is obtained as a by-product.

The manufacture of Potassium Chloride at Stassfurt.

At first the importance of the strata found underlying the rock-salt at Stassfurt was not recognised, and it is principally due to Dr. A. Franck since 1860 that this was ultimately done. In 1861 he erected a small factory, and was immediately followed by Messrs. Vorster & Grüneberg, and soon after by Messrs. Leisler & Townsend. The last-mentioned factory—called the 'English factory'—which was designed on the principle of introducing as much mechanical labour as possible in lieu of manual labour, was very important for the later development of that industry.

The raw material for the manufacture is the crude carnallite as supplied by the mines in

tolerably uniform quality; its average composition has been stated above. The principles of working it up are as follows: carnallite, $KCl,MgCl_2,6H_2O$, is unstable in the presence of water; it is decomposed into a magma of very finely crystallised potassium chloride and a solution of magnesium chloride, retaining but little KCl at a low temperature. On heating, the solution dissolves much more KCl, and on cooling the latter salt is separated in much larger crystals so long as the proportion of $MgCl_2$ does not exceed three times that of KCl. When that proportion has been reached the liquor on further concentration yields a crop of carnallite, which at a low temperature is very little soluble in the remaining solution of magnesium chloride. Of the foreign salts present in crude carnallite, rock-salt is much less soluble in hot $MgCl_2$ solution than KCl, and thus remains behind to a great extent; kieserite, which is insoluble as such but turns into soluble Epsom salts on heating with pure water, is prevented from so doing by the presence of magnesium chloride. The remaining substances are not of much consequence; some of them are quite insoluble.

Practically it has been found useful to treat the ground raw material, not with water, but with waste liquor from a previous operation in such quantity that it suffices for dissolving the carnallite present at a boiling heat; the solution is separated from the residue (the washings being utilised for a fresh solution) and is allowed to cool down, when it deposits about 80 p.c. of the potassium chloride; the mother-liquor, on further evaporation and cooling, yields the whole of the remaining KCl as a crop of carnallite which is decomposed by water as above. The products are purified in the manner described below.

The first operation, *dissolving the crude carnallite*, is the most important of all for the success of the manufacture. The result differs very much according to the quality of the crude carnallite, according to its state of division, according whether pure water or liquors obtained in other stages of the manufacture are employed, and also according to the duration of the operation. It is, in principle, preferable to effect the solution of carnallite as quickly as possible in order to dissolve less of the other salts. The quickest operation is undoubtedly that practised at the 'English' factory—crushing the crude carnallite into powder, and dissolving it in a close vessel at several atmospheres pressure with mechanical agitation. But this process causes too much rock-salt and even kieserite to be dissolved at the same time, and it also causes the formation of very much mud; hence most manufacturers work at the ordinary atmospheric pressure, or very little above it, without mechanical agitation, and employ coarsely-crushed carnallite.

Fig. 3 shows one of the usual descriptions of dissolver. The true bottom *g* is slanting, the false bottom *e* is horizontal. The latter is perforated by a large number of holes $\frac{1}{3}$-inch wide; in the centre there is a double-hinged trap-door *b*, also perforated. The two halves of this door are suspended from the hinged arm *a*; they are closed when *a* is in the upright position, in which it is kept by the vertical rod *h*. When the liquor has been run off through *c*, the man-hole *f* is opened and the rod *h* is knocked away, which causes the arm *a* to turn over, and the two halves of *b* fall down. The residue is now easily washed down from *e*, and cleared out through *f* by a strong jet of water passed all over *e* by means of a hose. The steam-pipe *d*, with two rows of holes, is carried round the central opening of *e*. The conical shape of the bottom has the two-fold advantage that the liquor can be run off completely and that the residue can be got out very quickly.

Formerly the dissolvers were made of wrought iron, but since it has been recognised that cast-iron resists much better the chemical action of the salts, it has become usual to employ cast-iron cylinders, with a conical bottom, provided with a sieve, below which the steam is introduced, the head of the steam-pipe being closed by a bulb with many perforations.

Where it is considered desirable to dissolve under a slight pressure, the top of the dissolver is covered in, the man-hole being closed during

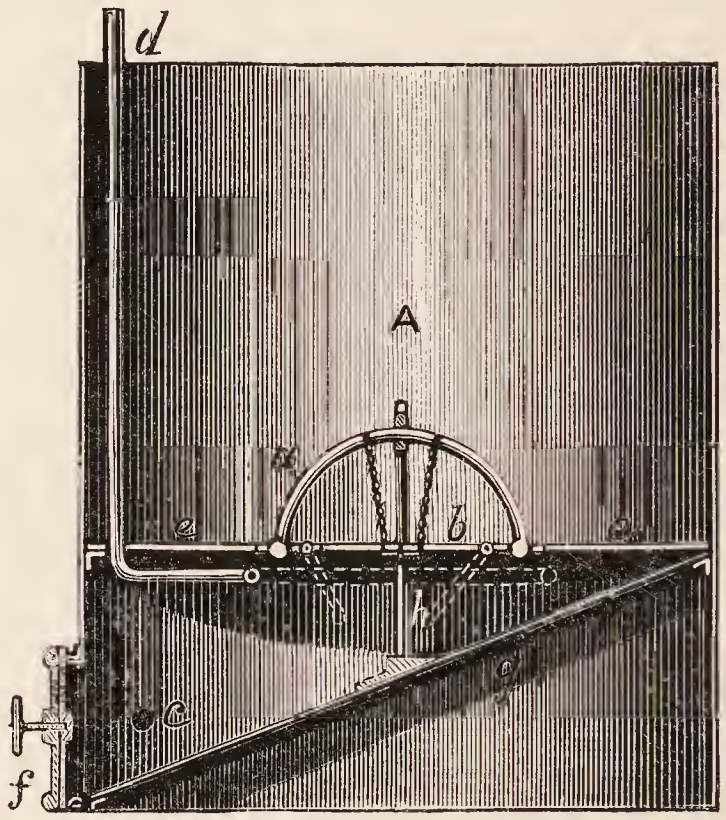


FIG. 3.

the work, or else a tube reaches down from the cover into the liquid, nearly to the false bottom, in order to introduce the salt, and to produce some degree of steam pressure in the apparatus. The waste steam can be employed for heating up the dissolving-liquor in another pan. Such vessels, of a capacity of about 350 cubic feet, admit of working up 50 tons of salt and more in 24 hours.

The liquor employed for dissolving (called 'Löselauge') is a mixture of various liquors resulting from the manufacture, especially the washings of the first residue, and those of the potassium chloride, as well as various mother-liquors, altogether of a sp.gr. 1·268 to 1·279; through being heated up by waste steam, the liquor is diluted to 1·257, and is used in this state. This liquor is run into the dissolver until this is half full; steam is injected until the liquor is raised to the boiling-point, and only then the crude carnallite is introduced. For each 100 cubic feet of tank room, from 30 to 36, or at most 42 cwt. of carnallite can be charged. The solution is first brought to sp.gr. 1·313 to 1·337

(measured hot and in the muddy state), but in this state the residue would be very difficult to treat; there would be considerable loss of potassium chloride by crystallising out before the liquor was clarified, and the potassium chloride obtained in the coolers would be contaminated by newly-formed carnallite. To avoid this, the solution is diluted to sp.gr. 1·28 or 1·30 (measured hot and muddy). The operation of dissolving ought not to last more than half an hour, or, including other necessary work, 2 hours, so that 12 operations can be made in 24 hours.

The solution must now be clarified by allowing it to rest for an hour or two in settling-vessels, and drawing off the clear portion by means of a drop-siphon. The clarifying operation can be promoted by sprinkling a little milk of lime on the surface, which precipitates some magnesia, the latter carrying down the other impurities. The residue must be once or twice boiled up with fresh water, if the crude carnallite had been employed in lumps of the size of a fist; if, as now usual, it had been more finely crushed, it is either removed at once, or it is previously boiled up with a small quantity of mother-liquor, the resulting liquor being utilised as part of the dissolving liquor for fresh carnallite, or by cooling down, when it yields weak potassium chloride.

The following analyses show the composition of the ultimate residue, formed from 26 to 30 parts of the crude carnallite:

	a	*b*	*c*
Potassium chloride .	5·25	3·0	2·2
Sodium chloride .	47·00	45·0	54·8
Magnesium chloride	3·85	2·0	2·5
Magnesium sulphate	29·25	38·0	22·9
Calcium sulphate .	2·15	0·7	1·8
Insoluble . .	6·00	5·3	5·0
Combined water .	6·50	6·0	10·8
	100·00	100·0	100·0

a is a product as formerly obtained, *b* and *c* more recent products of different works. The 'insoluble' is mostly anhydrous calcium sulphate, clay, boracite, and sand.

The residue was formerly allowed to accumulate in large heaps, part of which only was utilised for manufacturing kieserite and sodium sulphates; where there was not room enough for depositing it, it had to be washed away by a stream of water. Subsequently it was largely employed for filling up the old workings in the carnallite mines, since this was required by Government regulations in order to prevent subsidences of the soil.

A different kind of residue is obtained by thoroughly settling the liquid in tanks, protected against cooling, and drawing off the clear liquor by means of a drop-siphon. This second residue, the 'kieserite mud,' consists essentially of kieserite, accompanied by a little anhydrite, clay, boracite, gypsum, sodium chloride, &c.; also by potassium chloride. It is separated from the liquor by means of a vacuum filter, or, preferably, of a filter-press in which it can also be washed by hot mother-liquor, which removes the potassium chloride without affecting the other salts to a great extent. Even then from 4 to 26 p.c. of potassium, calculated as chloride, are retained in the mud, probably in the shape of potassium magnesium sulphate.

Formerly the clear liquor was purposely allowed to cool down to some extent, say to a temperature of 80° or even less, before being run into the crystallising vessels, in order to precipitate some sodium chloride. But since the solution is now made by means of mother-liquors, the clear liquor contains NaCl, and is generally at once employed for crystallisation. The following analyses refer, I. to a liquor made with water, of sp.gr. 1·3 (at 105°) in the muddy, and 1·284 in the clarified, state; II. to a liquor made with mother-liquor, of sp.gr. 1·313 (at 105°) before being diluted with water; III. shows the maximum and minimum percentages found in ordinary liquors:

	I.	II.	III.
Potassium chloride .	11·08	10·70	8–14
Sodium chloride .	5·68	4·20	4–8
Magnesium chloride .	17·65	24·60	15–25
Magnesium sulphate .	2·92	1·50	1·5–5
Water . . .	62·67	59·00	—
1 cubic metre contained . . .	142·2 kilo. potassium chloride.	140·5	

The crystallising vessels (coolers) are wrought-iron tanks of various sizes, usually from 150 to 300 cubic feet capacity—*e.g.* 7 × 8 × 4 feet, with bottoms slanting a little to one side, where there is a plug for running off the mother-liquor. They are best placed a little above the floor, so that the air can circulate underneath, and in summer this should be promoted by Venetian shutters in the building. If the cooling takes place too quickly, the crystals are too small and muddy. Two or three days ought to suffice.

The salt first precipitating carries down such suspended matters as had not been removed by settling; hence such 'bottom salts' are less pure than the 'side salts' crystallising afterwards. The quantity of the latter is sometimes increased by suspending bundles of wire in the coolers, but this is now done but rarely, as the extra labour is hardly recompensed by the advantages of that process. When the cooling has been finished, the mother-liquor is siphoned off, or is run off by a plug, exactly as in the manufacture of soda crystals.

The proportion of bottom salts to side salts ranges from 2 down to 1 part of the former to 1 of the latter; some analyses of this 'first product' run as follows:—

——	Bottom salts		Side salts		Mixtures of both
	Drained	Dry	Drained	Dry	
Potassium chloride	50·2	59·76	60·8	58·31	64–69
Sodium chloride .	27·0	32·14	24·4	27·42	28–22
Magnesium chloride	4·3	5·12	2·8	3·15	7·5–8·5
,, sulphate	2·0	2·38	1·0	1·12	0·5–0·5
Insoluble . .	0·5	0·60	—	—	—
Water . .	16·0	—	11·0	—	—

The mother-liquor drained off from the crystals of KCl retains about $\frac{1}{5}$ of the total KCl, most of which is recoverable by evaporation and cooling the concentrated liquor.

The following are analyses of the 'first mother-liquor,' as remaining behind from the

'first product' (I. former process, II. present process):

	I.	II.
Specific gravity at 20° .	1·273	1·279
Potassium chloride .	5·50	4·50 p.c.
Sodium chloride . .	3·80	3·20 ,,
Magnesium chloride .	19·90	22·80 ,,
Magnesium sulphate .	2·70	2·15 ,,
Water . . .	68·10	67·35 ,,

Part of it is employed for dissolving fresh crude salts as mentioned above; the remainder is concentrated by evaporation until nearly all the KCl can be obtained on cooling as artificial carnallite. This concentration was formerly carried out in two stages—first to sp.gr. 1·279 (when low-grade potassium chloride was obtained), and then to 1·325; but now, since coal is dearer and lower prices are obtained for the product, it is found best to concentrate at once to 1·325, which means evaporating about one-third of the bulk of the liquor, till the boiling-point reaches 123°.

The evaporation must be carried on in such manner that the heating surfaces are not covered by crusts of salts, and, of course, in such a way that the fuel is utilised in the best possible manner. Evaporating by means of steam-coils has been found less economical than by means of open fires. Passing over the antiquated modes of concentration as formerly employed at Stassfurt, we shall describe the more recent process. It is now usual to carry on the evaporation successively in two different kinds of apparatus—namely, first, up to the point where salts would be separated in the boiling liquor in ordinary two-flued steam boilers, the steam being utilised for dissolving and other purposes. In lieu of this the first stage is now usually, and with very great advantage, carried on in combinations of vacuum-pans, such as have been in use for a long time in sugar works, and here and there for caustic liquor. The second stage of concentration, where salts are separated during the process, is best carried on in open pans, heated

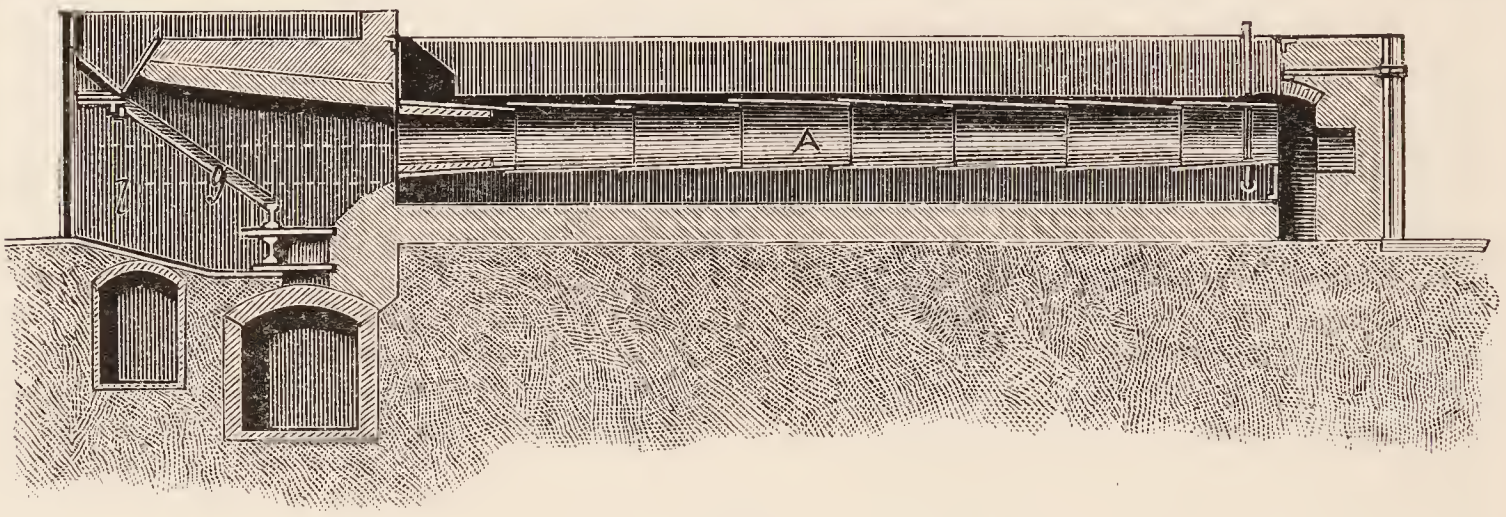


Fig. 4.

by internal flues, as shown on a scale of $\frac{1}{75}$ in Figs. 4 and 5, which at the same time illustrate the 'step-grates,' universally employed at Stassfurt for the friable brown coal found in the neighbourhood. The flame, generated on the grate *g*, passes through the central wrought-iron tube *a* and back again through the lateral tubes *bb* into the brick flues *ll*. The very strong boiling of the liquor prevents the formation of any crusts of salts on the tubes *a* and *b*.

It has now become general to cover in these pans, and to utilize the steam escaping from

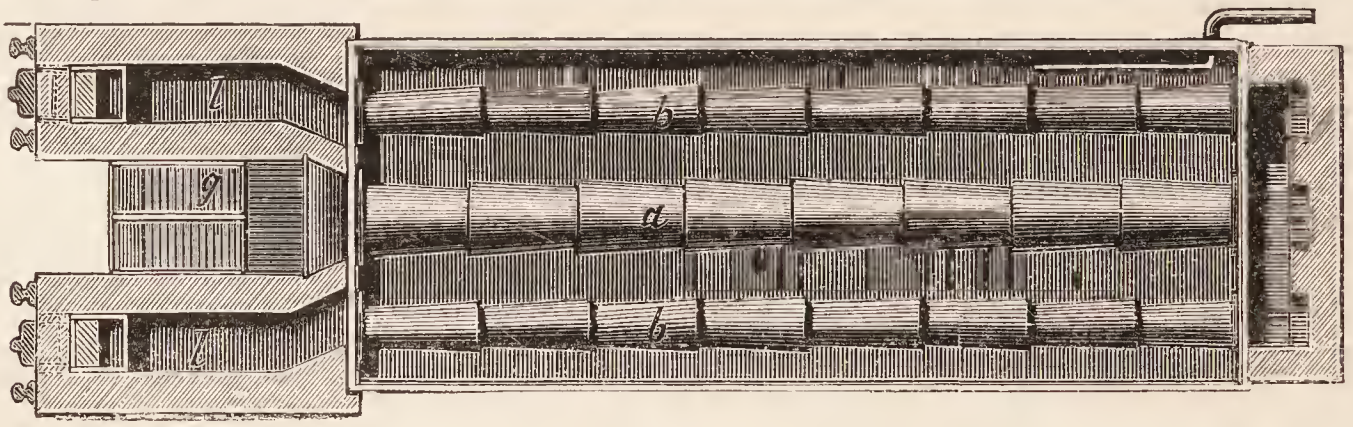


Fig. 5.

them in various ways. The consumption of fuel (lignite) has been greatly diminished by the introduction of gas-producers.

The first stage of evaporation, that in which no salts are separated, ends a little above sp.gr. 1·26; during this time the evaporation is continuous, fresh liquor being run into the boiler to keep it up to the same level. In the second stage the salts were formerly removed by fishing, which might be done more advantageously by mechanical means. It is, however, usual to boil down to sp.gr. 1·32 or 1·33 in winter, 1·33 or 1·345 in summer (testing the liquor in the muddy and hot state), to allow it an hour's settling, and to run it then into a cooler. The fished salts and the settling mud are washed with water, the washings being utilised for dissolving crude salts; but even then they contain from 7 to 12 p.c. potassium, calculated as chloride, together with 50 to 66 p.c. of sodium chloride, and cause an appreciable loss, as it is not easy to extract that potassium chloride with advantage.

The clear liquor contains about 5·5 to 6 KCl, 2–3·3 NaCl, 25–29 $MgCl_2$, 2·6–3 $MgSO_4$, and 59–64 H_2O. It is run into coolers, and left there

during three or four days. At first—that is, down to a temperature of 65°—principally sodium chloride crystallises out, and this can be kept out by a previous cooling down to that temperature. On further cooling, 'artificial carnallite' is separated, usually containing from 18 to 22 p.c. KCl, equal to 67–82 p.c. of real carnallite, together with a little NaCl, $MgCl_2$, and $MgSO_4$. This salt is dissolved in water, brought to boiling heat by means of open steam, till the sp.gr. = 1·268 (at 105°) has been attained, and a little milk of lime is added at the finish, in order to remove any iron present and to mechanically clear the liquid. The dissolving and settling last an hour each, the subsequent cooling three or four days. Sometimes the 'artificial carnallite' is decomposed in the cold way, by agitating it with cold water until most of the $MgCl_2$ is dissolved, and separating this solution by suction from the solid KCl remaining behind. The result of the operation is solid potassium chloride, 'second product,' and a 'second mother-liquor,' of sp.gr. 1·257 (measured cold) with 3–4 p.c. KCl, which is usually added to the first mother-liquor in the concentrating pans.

The quantity of second product amounts to about 20 p.c. of the total make of potassium chloride; its analyses show its comparative purity:

Bottom salts.

	Drained	Dry
Potassium chloride .	67·0	77·38
Sodium chloride .	13·7	15·82
Magnesium chloride .	5·3	6·11
Magnesium sulphate .	0·6	0·69
Water . . .	13·4	—

Side salts.

	Drained	Dry
Potassium chloride .	80·2	89·02
Sodium chloride .	7·0	7·77
Magnesium chloride .	2·6	2·88
Magnesium sulphate .	0·3	0·33
Water . . .	9·9	—

The following are tests of the 'final mother-liquor'—*i.e.* that which remains after the crystallisation of the artificial carnallite:

	Former process	Present process
Specific gravity . .	1·319	1·313
	———	–
Potassium chloride . .	1·25	1·20
Sodium chloride . .	0·95	1·20
Magnesium chloride .	29·50	28·05
Magnesium bromide .	0·30	0·31
Magnesium sulphate .	2·22	3·10
Water	55·78	66·14

Its quantity is 5 or 7 cubic metres to each 10 tons of crude carnallite, and it is now usually worked for *bromine* (*q.v.*); partly also for magnesium chloride (*v. infra*).

Purification of potassium chloride.—This is always performed by washing, utilising the fact that at low temperatures the solubility of KCl decreases very much more than that of NaCl, $MgCl_2$, &c., and that the contact of water with those salts itself causes a lowering of the temperature (sometimes amounting to 10°), so that the water in winter would be turned into ice if it were not employed in the tepid state.

The washing of the salt takes place in iron vessels, provided with a false bottom, upon which the salt rests. This false bottom is made of wood or of iron plates, perforated with $\frac{3}{8}$-in. holes, and is covered with sacking, or, preferably, with a web of split cane. The water or liquor employed for washing is sprinkled upon the salt by means of an elastic tube, ending in a rose, and the liquor is removed from underneath the false bottom by means of a tap or plug. In Fig. 6, A is the tub, *a* a man-hole through which the washed salt is removed at the end, *b* the false bottom, *c* the tube and rose for washing, *d* the charging bogie, *e* the running-off tap.

The tub is completely filled with salt, and this is first washed with washing-liquor from a former operation, which in this way yields some of the KCl previously taken up, and takes up

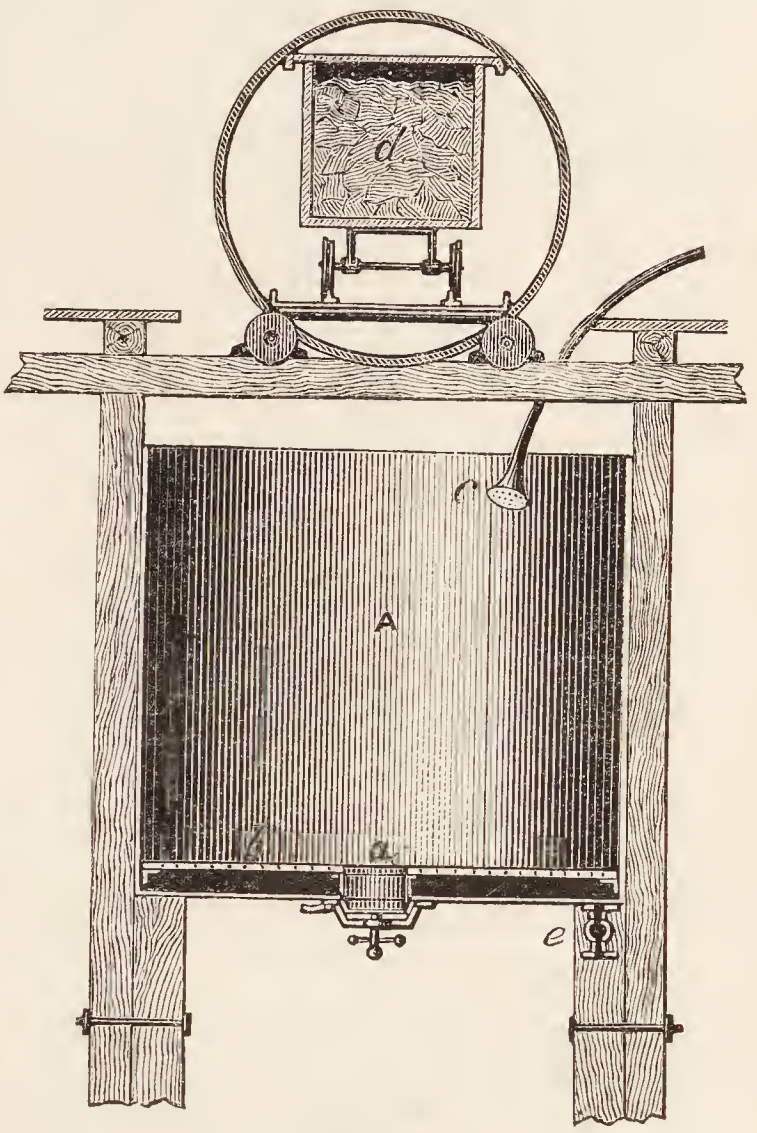


FIG. 6.

NaCl in this stead. After having twice served in this way, the liquor is used for dissolving crude carnallite, in the first operation described above. The first liquor is run off at once, until the mother-liquor has been displaced; the tap *e* is now closed, fresh liquor is run on to the top of the salt, leaving it in contact with the same for two hours, and then running it off. This is repeated with once-used liquor, and last of all with fresh water. The washing-tubs are best suspended from the staging by means of trunnions, with toothed-wheels for turning them on their axis at the end of the operation, for the purpose of emptying out the washed potassium chloride.

The washing operation is not advantageous with products containing less than 50 p.c. KCl; such products are better purified by re-crystallisation.

The washed salt naturally contains a considerable quantity of water. By simple draining this can be got rid of down to 7 or 9 p.c., by centrifuging to 5 p.c. The remainder is removed by heating, which was formerly mostly done in reverberatory furnaces. The apparatus in general use now is shown in Fig. 7 on a scale of $\frac{1}{50}$. Upon the foundation *i* a cast-iron drum *h* is mounted, the hollow part of which is heated by steam through *m*, whilst at *n* there is a steam-trap for the removal of the condensed water. In the centre there is a perpendicular shaft, *l*, revolving in a bearing protected by a cap. This shaft is moved by means of the pulleys *u* and the bevel wheels *k*, and it carries the horizontal arm *t*, to which are attached a number of plough-shares *a*, a crushing-roll *b*, and a discharging-scraper *c*, set in motion by handle *e* and lever *s*. The last-mentioned part serves at the end of the drying operation for moving the salt towards the circumference,

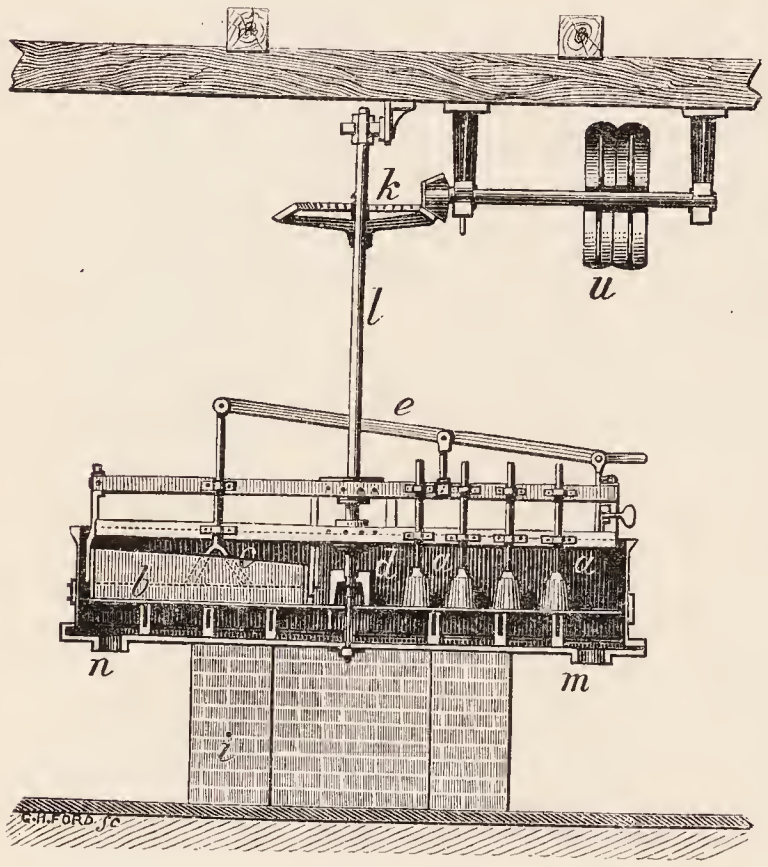


FIG. 7.

where it falls through an opening, kept shut up to this time by a slide, into a shoot and bag attached to it. Each charge yields 60 kilos. dry salt, and each drying-plate turns out from 2 to $2\frac{1}{2}$ tons per day of 27 hours. With wrought-iron plates of 8 feet diameter, which transmit the heat more easily, nearly 5 tons can be dried in 24 hours. In some places Thelen's mechanical drying-pans are employed, which are heated by direct fire, and yield about 15 tons per 27 hours, with an expenditure of 8 to 10 p.c. of brown coal (the fuel value of which is not quite one-half that of ordinary coal).

Whichever apparatus may be employed, the formation of crusts cannot be entirely avoided. These are removed once a day, and are crushed in order to be sold as manure salts, containing about 70 p.c. KCl.

The drying is usually carried up to 2 p.c. water for low grades, or 0·5 p.c. for high grades; but it is best to leave the salt a short time in a cool, dry place before packing. It is then crushed between rolls, sifted, and packed into jute bags, holding 100 kilos. each.

ANALYSES OF COMMERCIAL POTASSIUM CHLORIDE.

KCl .	80·85	89·78	82·00	96·5	84·30	98·58
NaCl .	16·25	8·10	16·00	2·0	12·98	0·22
$MgCl_2$	0·20	0·10	0·40	0·2	0·19	0·07
$MgSO_4$	0·59	0·33	0·30	0·2	0·10	0·12
$CaSO_4$	0·18	0·27	0·25	0·3	0·22	0·24
Insol. .	0·33	0·32	0·15	0·2	0·23	0·31
Water	1·60	1·10	0·90	0·6	1·98	0·46

Another process for treating carnallite has been patented by Schliephacke and Riemann (D. R. P. 43932). They smelt raw carnallite in a cupola furnace with felspar or granite, and run the liquid product into cold water, whereby it is granulated and the soluble salts are more easily extracted. Magnesium silicate remains behind in an insoluble state; the solution, which contains the potassium as silicate, is treated with a solution of crude carnallite or waste liquors from the manufacture of potassium chloride. The ensuing reaction is:

$$MgCl_2 + K_2SiO_3 = MgSiO_2 + 2KCl$$

so that only potassium chloride remains in solution. The gases escaping from the throat of the cupola furnace are to be treated for chlorine and hydrochloric acid. (This ingenious process does not seem to have been practically carried out.)

Manufacture of potassium chloride from sylvine.—This is an exceedingly simple matter, since a hot saturated solution of KCl+NaCl on cooling allows nothing but KCl to crystallise out. Ground sylvine is dissolved in the same way as described in the case of carnallite; the solution, if necessary, is cleared by subsidence and allowed to crystallise, just as the solutions obtained from carnallite. The resulting potassium chloride tests 92–94 p.c. KCl, even without washing, and by washing can be brought up to 98 p.c. Experience has shown that the crude sylvine should not contain more than $\frac{3}{4}$ p.c. MgO (in the shape of kieserite); if it contains more, both MgO and SO_3 are removed by adding milk of lime. A modified process for obtaining sylvine from mixtures with rock-salt, &c., is described in the D. R. P. 132474 of Speyerer.

The manufacture of KCl from *hartsalz* is carried on in a similar manner, *e.g.* by Tünger's D. R. P. 102075; but as this material is of very varying composition, the special rules for working must be fixed from case to case.

Meyerhoffer (D. R. P. 91906) obtains potassium chloride from carnallite by heating this to about 167°. About three-quarters of the KCl is thus obtained in a solid form, whilst the remainder and all the $MgCl_2$ remains in solution which, on cooling down to about 115°, deposits nearly all the KCl and leaves only $MgCl_2$ in solution. The same inventor (D. R. P. 92812) purifies carnallite by heating to about 265° and removing the fused carnallite by presses from the residue. Further improvements are described in his D. R. PP. 98344, 99957, 109101.

The Salzbergwerk Neustassfurt (D. R. P. 138562) dissolves the carnallite *in situ* underground by means of tepid water, the solution being pumped up.

Maurer (D. R. P. 166558) gives detailed prescriptions for the preparation of potassium chloride from the crude Stassfurt salts.

Haag and Glienicke (D. R. P. 163413) fuse the carnallite out of the crude salts by electric heating.

By-products of the Stassfurt potash industry.

1. **Kieserite.** This insoluble body $MgSO_4,H_2O$ which becomes soluble only by prolonged contact with water, when it passes over by an intermediate stage into Epsom salts $MgSO_4,7H_2O$, is naturally left behind in the residues from dissolving crude carnallite and settling the liquor. Most of it is lost in the shape of pit heaps, &c.; only then is it regularly recovered by the potash manufacturers, when they are obliged to get rid of their residues by washing away, because in this case the law compels them to retain the insoluble portions; otherwise kieserite is only prepared when there is special demand for it. Since it soon passes over into the above-mentioned intermediate stage, it must be made from fresh residues, which is done by subjecting them to a combined levigating and sifting process. A convenient apparatus for this purpose is shown on a scale of $\frac{1}{50}$ in Fig. 8, where *g* is a hopper containing the residues, which rest on a grating; the water issuing from *b* produces a muddy liquor, which meets the slanting sieve *c*; the coarser portions run off at *f*, the finer ones pass through into the slanting shoot *d*, where at first anhydrite is deposited, whilst further on, at *e*, kieserite is found. The clay, together with a little boracite, remains suspended till the last, and is kept back in special settling basins. Of course, in lieu of the slanting shoot *d*, several settling troughs with overflows can be employed.

The kieserite must be removed at short intervals and put into iron or wooden moulds, where it solidifies after fifteen minutes, so far that the blocks can be taken out. The solidification (which is a process similar to that occurring with gypsum, a chemical combination with water taking place) proceeds with evolution of heat; in a few days the blocks, weighing $\frac{1}{4}$ to $\frac{1}{2}$ cwt., are as hard as stone, and can be sent out in this state without being packed in casks, bags, or the like. After a lapse of time, however, they fall to powder by the attraction of atmospheric moisture and formation of Epsom salts.

The quality of block kieserite naturally varies, according to the more or less careful separation from other matters; a minimum of 55 p.c. magnesium sulphate is frequently guaranteed. When it is required in the ground state, it is first calcined in a reverberatory furnace.

Analyses of Kieserite Blocks

	Fresh		Calcined	
Magnesium sulphate . .	60·20	58·0	81·5	77·8
Sodium chloride .	1·55	2·1	2·1	2·7
Insoluble (anhydrite, &c.) .	10·63	13·5	14·4	17·0
Water . .	27·62	26·4	2·0	2·5

The yield of block kieserite is about 10 p.c. of the crude carnallite. With careful work it can be got up to 12 p.c., but this is scarcely ever done, because at present only one-tenth of the residues is worked for it, the demand not being equal to the supply.

A small quantity of block kieserite is converted into *calcined kieserite*, with a guaranteed minimum percentage of 70 p.c. $MgSO_4$, by calcining in ordinary reverberatory furnaces, grinding and packing in bags.

The Gewerbschaft Carlsfund (D. R. P. 166187) obtains kieserite from its mixture with common salt by digestion with more or less concentrated salt solutions.

Applications of kieserite.—Most of it is employed for making Epsom salts, some of it for potassium sulphate. We mention the following attempts at utilising the substance in other ways.

G. Clemm (in 1863) calcined the kieserite, preferably mixed with coal, in the presence of steam, and carried the vapours into vitriol-chambers; magnesia remains behind (in a very impure state). By a similar porcess Precht (in 1881) makes basic linings for the steel process. Several other inventors have tried to utilise either the sulphuric acid or the magnesia.

The only extensive employment of kieserite is that of converting it into *Epsom salts*, of which about 25,000 tons per annum are made in Germany, and a considerable quantity in England and in the United States. The process consists simply in causing the kieserite to take

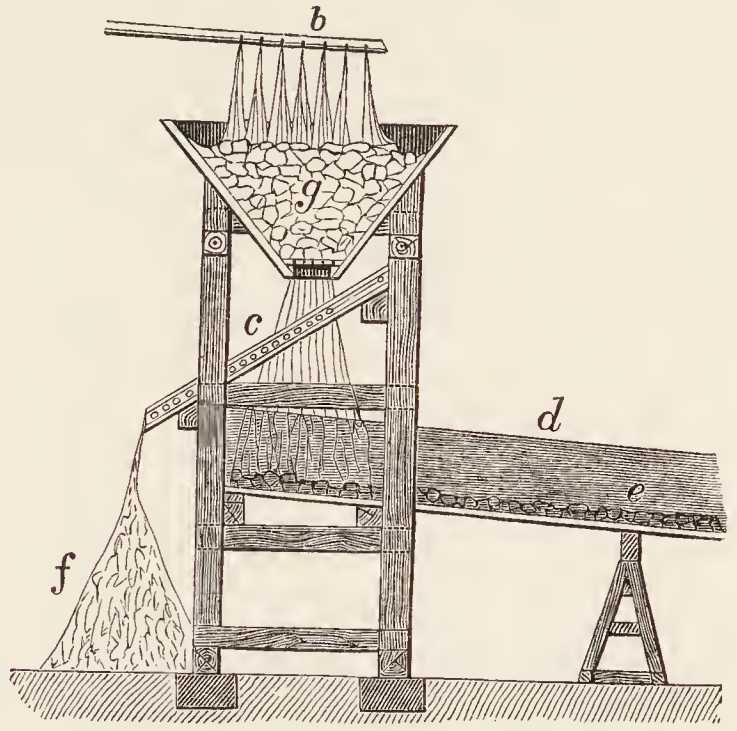


Fig. 8.

up more water, preparing a solution, and allowing this to crystallise. Formerly the process was promoted by calcining the kieserite, after which it is at once soluble in water; but this object can be equally attained by the prolonged application of steam, or, even more cheaply, by soaking the crushed kieserite with the mother-liquor from the Epsom salts, when it gradually passes over into the heptahydrated salt, with great increase of bulk. A solution is now prepared by water and steam, of sp.gr. 1·31 to 1·325 (tested hot and muddy). This is clarified in settlers, where it is kept about an hour; the last particles of gypsum and clay, floating in the liquor, are removed by wood-lined filter-presses; the purified solution (if necessary concentrated in lead-lined pans by means of lead coils) is run into lead-lined iron or wooden crystallising vessels.

After three or four days the crystallisation is finished; the crystals are all the finer the more concentrated the liquor had been, and they are at first practically free from sodium chloride. By concentrating the mother-liquor inferior qualities are obtained; the last liquor is run to waste.

The crystals of Epsom salts are in England merely drained by a centrifugal machine, turning

out 2 tons per day, and the product, still containing 3 or 5 p.c. of moisture, is directly packed into casks; in Germany they are dried in a room heated by exhaust steam, &c., at a temperature not exceeding 45°, the dry salt is passed through wooden rollers, leaving a space of $\frac{3}{8}$ inch, so that only the lumps are crushed; it then passes through a sieve, and from this into the casks.

The favourite shape of Epsom salts is that of fine needles, of silk-like lustre, which are most easily formed by moderately quick cooling of a concentrated solution. The coarser crystals are separated by sifting and re-dissolved, or sold as second quality.

The principal application of Epsom salts was formerly the medicinal one, which, of course, did not amount to large quantities. At present the greater portion of it is employed in finishing textile fabrics, especially calico. Other applications (mostly only proposed or temporarily tried) are those for replacing the 'pearl-hardening' in paper-making (mixed with lime), for preparing precipitated barium sulphate, for purifying beet-root sugar juice, for rendering fabrics fire-proof, for manufacturing sulphur trioxide, in several soda-making processes, and so forth.

2. **Glauber's salt** $Na_2SO_4,10H_2O$, can be made by Balard's process—that is, exposing a mixed solution of sodium chloride and magnesium sulphate to a temperature below 0°, when the following reaction takes place:

$$2NaCl+MgSO_4+10H_2O=MgCl_2+Na_2SO_4,10H_2O$$

The Glauber's salt crystallises out, magnesium chloride remaining in solution. At the mouth of the Rhone this is done by artificial cold; at Stassfurt it can be done without that during the winter months. The material is present in the residues from dissolving crude carnallite, the composition of which has been stated already.

The residue is dissolved in various ways; the longer it has been exposed to the weather, the more easily the solution takes place. Usually the residue heaps are lixiviated on the spot by means of hot water, the solution being caught in a trench made at the bottom of the heap. If the proportion is not $=2NaCl$ to $1MgSO_4$, the composition of the liquor is corrected and its strength is brought up to about 1·269 at 33°. The solution is clarified by settling, and is exposed to the cold of a winter's night, always under the open sky. Ordinary coolers are not so well adapted to this purpose as large, shallow tanks, made of pine-wood planks, the joints being made tight by caulking with hemp and tar. These tanks are erected on wooden pillars, and are sometimes 100 by 100 feet square, and 8 inches deep. During summer, when they are not used, they are kept filled with a solution of common salt. In such shallow tanks the liquor is better cooled down during the night, 1 cubic metre often yielding 150 to 180 kilos. of crystals. The mother-liquor is run off in the early morning, before it can get warm again; it shows the sp.gr. 1·205 to 1·225.

3. **Magnesium chloride** $MgCl_2,6H_2O$, is obtained by evaporating the 'final mother-liquor' in the same description of apparatus as described above for the treatment of carnallite liquors, usually in pans with flame-pipes, to a b.p. of 157° which corresponds to sp.gr. 1·388 or 1·40 (taken hot), allowing to settle for an hour, and running into a cooler, whereupon the whole mass solidifies in a few days. It is broken into large pieces, which are put into casks; the empty space is filled up by a hot, strong solution of magnesium chloride, which on cooling, cements the whole into a solid mass. A colourless, glassy product is obtained by boiling down only to sp.gr. 1·44, oxidising the ferrous salts by adding potassium chlorate (of which about 3 kilos. is required for a charge of 40 cubic metres of concentrated solution), heating further until a b.p. of 157° has been reached, and precipitating the iron by the addition of an excess of milk of lime (of which about 130 kilos. CaO will be required for 40 cubic metres of liquor), and cooling down to about 125°. The liquid is then run through the bung-hole into petroleum casks, in which it solidifies, and is sent out in this state. The analyses show:

	Boiled down to sp.gr. 1·388	Boiled down to sp.gr. 1·4
Magnesium chloride .	45·74	51·05
Potassium chloride .	1·35	1·38
Sodium chloride .	0·25	0·27
Magnesium sulphate .	0·15	0·10
Water . . .	52·51	47·20

The material is principally employed for dressing (lubricating) the warp in weaving calico. A very large number of further applications have been proposed, in order to utilise either the chlorine, or the magnesia, or both. We mention here the following applications: as a disinfectant; for precipitating waste soap-lyes; for carbonising wool; for making patent fuel; for magnesia cement; for preparing magnesia, principally as 'basic lining' in the manufacture of steel; for manufacturing barium chloride.

Crystallised magnesium chloride is made by evaporating only to sp.gr. 1·42 and pouring the liquor into casks, already containing blocks of $MgCl_2$ crystals, between which it solidifies. The crystal cakes contain about 43·0 p.c. $MgCl_2$, 1·3 KCl, 1·2 NaCl, 3·4 $MgSO_4$, 51·1 H_2O.

Magnesia alone is made from magnesium chloride liquor by means of lime, in two stages, viz. first, precipitating the sulphuric acid and iron, if necessary with addition of a little bleaching powder and removing the precipitate; second, adding more lime to decompose the $MgCl_2$ into MgO and $CaCl_2$.

4. **Bromine** is largely made from the final mother-liquor of the Stassfurt works, which contains about 0·25 or 0·29 p.c. of it in the state of $MgBr_2$; *cf.* the article BROMINE.

Part of the $MgBr_2$ is converted into the iron compound Fe_3Br_8 and sent out in this state to the bromine works, or into the bromides of potassium, sodium, and ammonium.

5. **Boracic acid** is made from boracite or stassfurtite, $2Mg_3B_8O_{15},MgCl_2$, of which several hundred tons per annum is obtained at Stassfurt. It is dissolved in concentrated hot hydrochloric acid; the clarified solution is run into wooden coolers, lined with lead, where boric acid crystallises out. The crude acid is purified by washing or recrystalling. 100 parts of commercial boracite yield about 82 to 85 parts of crystallised boracic acid H_3BO_3, which is partly sold as such, and partly converted into borax (*q.v.*).

6. **Potassic manures** (*artificial fertilisers*) are

made from all the by-products of the Stassfurt manufacturers, as well as from minerals specially got for this purpose, especially kainite. The manufacturing operations consist merely in grinding, drying, calcining, and effecting a proper mixture to bring the product up to the guaranteed percentage of potash. Potassium sulphate is much better for this purpose than chloride, and magnesium chloride in the free state is absolutely injurious to vegetable life. Hence kainite and schoenite (*cf. Potassium sulphate*) are most usually employed as manures; but low-grade potassium chloride is also frequently sold for this purpose (*v.* FERTILISERS).

Figures published by the 'Kaliprüfungsstelle' give the German production of potash salts in 1921 as 9,241,179·4 metric tons (1,066,848·7 t. K_2O), the decrease of 2,145,259·4 t. as compared with 1920 being due to the lack of demand during a great part of the year. The production in 1921 was dsitributed as follows: Hanover, 2,912,997·1 t. (334,426·1 t. K_2O); Stassfurt, 1,989,829·5 t. (215,499·4 t. K_2O); Halle-Mansfeld-Unstrut, 1,134,794·1 t. (114,389·7 t. K_2O); Süd Harz, 1,746,430·6 t. (231,719·8 t. K_2O); Werra, 1,457,128·1 t. (170,818·7 t. K_2O). Production and sales of potash products during 1921 were as follows:—

		Metric tons	
		Production	Sales
Crude salts	12–15 p.c. K_2O	1,985,757·9	2,064,122·7
Carnallite	9–12 ,, ,,	262,675·2	27,755·2
Manure salts	18–22 ,, ,,	329·081·3	343,293·6
,, ,,	28–32 ,, ,,	88,693·2	88,453·6
,, ,,	38–42 ,, ,,	752 312·2	800,194·2
Potassium chloride	56–60 ,, ,,	354,435·5	365,990·2
do.	over 60 ,, ,,	77,655·8	
Potassium sulphate	over 42 ,, ,,	44,628·0	43,512·3
Potassium magnesium sulphate		11,709·1	12,213·0

The total sale for the year was 3,745,554·7 t. of potash salts (921,564·6 t. K_2O), of which 3,181,530·2 t. was disposed of in Germany. Exports amounted to 564,024·5 t. (152,838·1 t. K_2O), a slight improvement compared with 1920. By a contract made in October, German potash salts were again placed on the United States market, and Holland, Scandinavia, England, Austria, and Czechoslovakia began to purchase. Competition was felt, especially in the American market, from Alsatian potash, of which the output totalled 895,744 t. of crude salts (146,355 t. K_2O) in 1921 (Journ. Soc. Chem. Ind. 41, 1922, 178 R.).

According to official statistics the German output of potash during the first half of 1922 was 5,893,711 metric tons of potash salts, equivalent to 682,787 tons of pure potash (K_2O). Details of the production and inland sales of potash salts (calculated as K_2O) are as follows:—

	Production Jan.–June, 1922		Inland sales
Carnallite	22,739		1·34
Crude salts	139,710		137·92
Manure salts	(18–22 p.c.)	39·20	18·61
,, ,,	(28–32 ,,)	10·35	16·02
,, ,,	(38–42 ,,)	241·34	245·47
Potassium chloride	(50–60 ,,)	90·78	102·91
,, ,,	(over 60 ,,)	37·80	
Potassium sulphate	(over 42 ,,)	17·11	3·98
Potassium magnesium sulphate, calcined		6·25	0·46

J. Soc. Chem. Ind. 1922, 41, 569 B).

POTASSIUM CHLORIDE FROM ALSACE.

Next in importance to the potash deposits of the Stassfurt district—possibly of even greater ultimate importance—are the deposits of a district in Alsace, of which Mulhouse is the centre. They were first discovered in 1904 and were only partially developed by the Germans prior to the Great War, but, now that Alsace is once more in the hands of France, their development is likely to be rapid and of great extent. For an excellent account of them, accompanied by a map, *see* Kestner (J. Soc. Chem. Ind. Nov. 15, 1918).

The potash exists in two beds, of which the lower is the more important of the two, has an average thickness of 4 metres, and occupies an area of 200 square kilometres at a depth of from 650 to 1000 metres. The upper bed is not so thick, but runs fairly parallel to the lower bed from 15 to 25 metres above it. The average content of the upper bed is from 30 to 35 p.c. of potassium chloride, and the lower from 22 to 25 p.c., and an approximate analysis of each is as follows:—

Upper bed: (Silvinite 20–22 p.c. K_2O) KCl 32–35 p.c., NaCl 50–55 p.c., $CaSO_4$ 2–5 p.c., insoluble matter 9–10 p.c.

Lower bed: (Silvinite 14–16 p.c. K_2O) KCl 22–25 p.c., NaCl 63–66 p.c., $CaSO_4$ 2–5 p.c, insoluble matter 10–12 p.c.

The average potash contents of the whole deposit are believed to be approximately 17 p.c., expressed as K_2O.

Above the upper bed is a layer of rock-salt intermingled with clay and shale, similar strata being found between the two beds of potash, and these hard layers of clay and shale form hard and water-tight roofs for the mining of the potash. This is, comparatively speaking, a simple operation, provided that water is kept out of the mines, and to achieve this end great care is taken, the shafts being lined with cement or sheet-iron castings. From the bottom of these shafts galleries are pushed right through both of the potash strata and form the main arteries of the mines, along which trolley lines are run and electric cables laid to supply power for the workings. As a rule both potash beds are worked simultaneously, the upper slightly in advance. The saps branch off from the main gallery, and from each of these approximately 50 tons of potash salt per day is extracted.

The method of extraction is that common to most mining operations, namely, by blasting and the removal of the material that is broken up by the explosion. The saps are of considerable height and are worked into large excavation rooms to about 40 feet in length, with solid pillars of salt between to give support to the roof. The material is loaded in the sap into trolleys, which are then taken along the main galleries to the bottom of the shaft and raised in elevator cages to the surface, and from them the mineral is tipped into crushers and is ready for distribution from the crushers as manure salt.

Owing to the fact that the potash from the Alsatian deposits does not contain those soluble impurities which are found in the Stassfurt deposits (*v. supra*), the production of commercial potassium chloride from it can be

effected by simpler and less costly operations. In the process of purification advantage is taken of the fact that the solubility of potassium chloride in hot water is greater than in cold water, while that of sodium chloride varies little with the temperature of the solution, and the process adopted at all the mines is practically identical, with but slight modification in details of plant, the main difference being that the solution tank in some cases works continuously and in others intermittently. In both cases the crushed potash salts are fed direct into a tank containing a hot, saturated solution of sodium chloride, which passes continuously through the whole system from the solution tanks to the crystallising tanks and back again.

The density of this hot sodium chloride solution on entering the solution tank should be 1·23 and on leaving it should be 1·26, and the temperature of the solution in the tank is maintained at between 105° and 110°C. by steam coils.

In the continuous system the solution tank is rectangular, about 25 feet by 6 feet, with a conveyor along the major axis which passes the salts along the tank through the solution against its flow, the rate of which is so arranged that all the potash is dissolved before leaving the tank. Some 25 to 30 tons of salts can be treated hourly in a tank of this size.

The intermittent system is operated in circular tanks about 10 feet in diameter and 10 feet deep, with a false bottom for draining the solid residual perforated with ½-inch holes and heated either by steam coils or direct steam heating. From these tanks the solution is run off and the solid deposit of sodium chloride and clay drawn off from the bottom filter and washed, and then used as a filling for the mine workings. From this point the production of potassium chloride becomes identical in both systems, the hot saturated solution containing potassium and sodium chlorides passing from the solution tanks into settling tanks, where the temperature of the solution is allowed to fall to about 70°C. and the clay and other solid matters are deposited. The clear solution, containing about 37 p.c. potassium chloride, is then run to the crystallising tanks and left for two or three days, and in these tanks the potassium chloride crystallises out on the sides and sodium chloride, with traces of clay, on the bottoms of the tanks. The solution containing sodium chloride and slight traces of magnesium salts is then pumped round to be re-heated and passed back to the solution tanks, the loss due to evaporation, &c., being made up by the washings from the filtrate from the solution tank.

The potassium chloride is graded in purity from top to bottom of the sides of the crystallisers, and, when silvinite from the upper bed of the deposit is used, potassium chloride can be recovered from the upper part of the crystallising tanks of sufficient purity to contain upwards of 95 p.c. KCl, and indeed if the proper precautions are taken as much as 98 p.c. KCl of potassium chloride may be obtained in the dried salt after careful selection from the sides of the tank. Generally speaking, the crystals are raked out all together from the sides of the tank on to a conveyor, which passes through a drying oven about 40 feet long and 5 feet in diameter, fitted with a spiral ledge to convey the salt through the oven. Hot gases are pulled by the oven over the salt through the cylinder, and the dry salt, containing from 85 to 90 p.c. of KCl, falls from the drying oven into a worm conveyor which feeds it to an elevator, by which it is carried to storage bins. An important factor in the production of potassium chloride from silvinite is the comparative absence of soluble impurities which permits of the mother-liquors being utilised for a long period.

The process as described above, which is that now operated in Alsace, has been shown by experience to be capable of modification to advantage in certain respects. The difficulty is one of settling the strong solution before it has time to cool, and it has been found that by the adoption of suitable methods a perfectly clear solution can be obtained in the solution tank without recourse to settling tanks and without permitting the temperature of the solution to fall below 95°C. This solution is run into agitated crystallising pans, and in 24 hours a clean white crystal is deposited containing, when dry, from 85 p.c. to 90 p.c. of potassium chloride.

A complete analysis of a sample of silvinite gave the following numbers :—

KCl	29·84 p.c.
K_2SO_4	2·08 ,,
NaCl	55·66 ,,
$CaCl_2$	1·46 ,,
MgO	slight trace
Insoluble	9·39 p.c.
H_2O	1·42 ,,
	99·85 ,,

and an analysis of potassium chloride manufactured by this process from this silvinite was as follows :—

KCl	84·52 p.c.
NaCl	8·88 ,,
H_2O	6·50 ,,
Sulphate	trace
	99·90 ,,

The acquisition of Alsace by France has broken the German world monopoly of potash. The increase in the exports of potash (K_2O) from Alsace between 1913 and 1920 in metric tons is shown below :

	1913	1919	1920
France	10,278	48,958	86,578
Germany	13,743	13,743	13,743
United States	12,185	26,702	55,967
Great Britain	219	4,499	17,890
Belgium	614	4,414	19,750
Other countries	3,682	9,157	18,990
Total	40,721	93,730	199,175

Potassium chloride from the mother-liquors of the manufacture of sea-salt.—The utilisation of the mother-liquors, obtained in the manufacture of sea-salt by evaporation in the ' salt gardens,' has been worked out at Giraud-en-Camargue, at the mouth of the Rhone, originally by Balard, later on by Merle and Pechiney. Descriptions

of this industry have been given by Wurtz (Hofmann's Bericht über die Wiener Ausstellung, 1875, [1] 410) and Lunge (Chemische Industrie, 1883, 225). We quote here only those portions referring specially to potassium chloride.

From each cubic metre of sea-water, after obtaining the salt, 64 litres of mother-liquor, testing 27°Bé., remain behind. This mother-liquor is concentrated by solar heat to 32½°Bé.; the salt crystallising out during this operation is of inferior quality (down to 91 p.c. NaCl), and is not utilised at Giraud. But on further evaporating, by solar heat, from 32·5° to 35°Bé., a mixture of sodium chloride with nearly its equivalent of magnesium sulphate is separated, which is known as 'sels mixtes,' and is worked up in various ways, especially for Glauber's salts, by artificial cold. The liquor of 35°Bé. is kept during the winter in very large and deep tanks, where the temperature is prevented from falling below 12°C., when only Epsom salt crystallises out, but no carnallite. The new mother-liquor, testing 33°Bé., of which 16 litres per cubic metre of sea-water has remained, is further evaporated by artificial heat in a Porion's furnace until it shows 37°Bé., tested hot. On the other hand, magnesium chloride solution, obtained at a later stage as a by-product, is evaporated in ordinary open pans to 40°Bé. Both hot liquors are run at the same time into an iron mixing-pan, taking care to maintain an excess of magnesium chloride. This causes at once a considerable separation of 'sels mixtes,' which are removed by a dredging apparatus. The hot liquor remaining behind still contains all the potassium salt; this is, however, separated on cooling in the form of artificial carnallite, owing to the presence of so much magnesium chloride, most of which is left in the cooled-down mother-liquor. This artificial carnallite, being in the state of fine mud, is easily decomposed by agitation with cold water, when magnesium chloride enters into solution and potassium chloride is left behind in the solid state. By systematic washing the latter can be brought up to 82 p.c. KCl.

Potassium chloride from lake brines.—The occurrence of potassium salts in the U.S. salines is described by Turrentine (U.S. Dept. Agri. Bulletin, No. 94, 1913), and potassium chloride is now recovered on a commercial scale from lakes in Nebraska and Searles Lake in California.

Searles Lake is completely covered with a thick crust of crystal, and for the recovery of potash this crust is pierced and the brine pumped from underneath, the crust being about 20 feet thick. The brine contains potassium and sodium chloride and borax in considerable quantity, with smaller quantities of sodium carbonate and sulphate, a little magnesia and other impurities. It is pumped into large storage vessels and passed by gravity through coils placed in the concentrated liquor pans, thus serving to heat the brine and cool the concentrated liquor to the point of crystallisation. The heated brine is pumped into a series of vacuum evaporators, each of which is 86 feet high by 26 feet in diameter, and contains 3½ miles of tubing 2½ inches in diameter. A propeller agitator works in each of these vessels above the tubes, and the salts deposited prior to the crystallisation of potassium chloride are removed by bucket elevators. These early saltings contain chiefly carbonate, sulphate, and chloride of sodium. The three evaporators are worked in series, so that the steam evaporated from No. 1 serves to heat No. 2, and that from No. 2 to heat No. 3, the steam from No. 3 effect being condensed by a jet condenser. The liquor from the final vessel is pumped to a vat and cooled by the cold brine to 4·5° (40°F.), about 90 p.c. of the total potash being deposited at this point while the remaining 10 p.c. and the borax goes forward.

By further cooling the liquor to −1° (30°F.) the potash and practically all the borax are thrown down.

The first crystals are washed in a centrifugal separator and sold as potassium chloride, while the second crystals are treated with cold water, when the potassium chloride is dissolved and separated from the borax in a continuous filter press, the potassium chloride being crystallised out for sale as such.

The crude borax is dissolved in hot water and the hot liquors specially treated to remove traces of organic compounds, as these discolour the borax, which is, after their removal, crystallised out and packed for sale.

Potassium chloride from kelp.—In the manufacture of iodine from kelp—that is, the ashes of sea-weed—as obtained on the coasts of Scotland and Normandy, a large quantity of potassium salts is obtained, which, previously to the working of the Stassfurt deposits, was one of the principal sources of these salts for technical purposes. The liquor obtained by lixiviating the kelp is concentrated by evaporation in several stages, and thus yields several crops of crystals. The first crop, called 'plate sulphate,' is a mixture of potassium sulphate with some sodium sulphate and common salt; the mother-liquor yields, on further evaporation while hot, a mixture of common salt with alkaline sulphates and carbonates, which is fished out from the pans and sold as 'kelp salt'; on cooling, a crop of potassium chloride is obtained. The latter can be brought up to upwards of 90 p.c., and formerly about 2500 or 3000 tons of it was made per annum; but the development of the Stassfurt industry has mostly compelled the iodine manufacturers to give up the separation of the potassium salts in the pure state, and to utilise the rough mixture of those salts for agricultural purposes.

During the Great War a large plant was installed in California for the treatment of kelp for the production of acetone with potassium chloride as a by-product. The process adopted was as follows: Seaweed was cut by a Harvester boat, chopped up and loaded into barges, from which the material was pumped direct into large vats of 50,000 gallons capacity each, 8 feet of seaweed pulp and 4 feet of water comprising the charge. These vats were agitated by means of air, and at the end of 18 hours 1000 lbs. of ground limestone added and a similar amount 24 hours later. The sludge was allowed to stand for 18 to 25 days and pumped to a steriliser, where it was heated. Just before it reached boiling-point slaked lime was added and the mass boiled for 15 minutes and pumped to wooden vats of 60,000 gallons capacity. After settling, the liquor was decanted

and the mud passed to a counter-current washing system and filter-pressed. The liquors were concentrated by vacuum evaporation and finally cooled in three stages, calcium acetate, sodium chloride, and potassium chloride being salted out in the various stages, the latter being of high quality, averaging 95 p.c. KCl.

Acetone was manufactured from the calcium acetate and iodine recovered from the final mother liquors, while the residue from the filter presses was sun dried and sold as a fertiliser. In view of the fact that on the termination of the war the plant was closed down permanently, this process is not here described in more detail, as it is now known that its main objective was the manufacture of acetone (Chem. & Metal. Eng. 1918, xviii. 11).

Potassium chloride from blast-furnace gases.—Chance (J. Soc. Chem. Ind. 1918, xxxvii. 222) has shown that by the addition of salt to the blast furnace charge, potassium chloride is volatilised into the gas to the extent of from 40 p.c. in the case of Cleveland ores to 80 p.c. in Northamptonshire and other ores (Rossiter and Dingley, J. Soc. Chem. Ind. 1919) of the potash available in the ores charged to the furnace, 1 lb. KCl being volatilised for each 1 lb NaCl added to the charge. The gas is then passed through a cleaning plant, wherein the dust and potash are extracted and clean gas passed forward for use in gas-engines or under boilers.

The type of cleaning plant which has been most successful in this country is that known as the Halberg-Beth, whereby the gas is passed through long cylindrical tubes made of flannel or cotton, which are periodically cleaned by shaking and at the same time blowing the gas through the walls of the tube in the reverse direction.

In the U.S.A. a similar result has been achieved, though not altogether successfully in the case of blast-furnace gases, by the Cottrell system of electrical precipitation, and an attempt has been made in this country to develop this method of gas cleaning *v* Precipitation, Electrical.

The residual dust, which contains potassium salts to the extent of from 25 p.c. to 60 p.c., the major part being chloride, is then taken to a refining factory and lixiviated. The impurities found are of two classes, carbonates and traces of cyanides, ferrocyanides and sulphocyanides being found in the one class while the other contains chlorides of calcium and iron. By mixing these two classes of material in the lixiviation vat the surplus chlorides react with the potassium carbonate to form potassium chloride and, in the absence of alkali, the cyanide and ferrocyanide are precipitated with an iron salt as ferrocyanide of iron. The liquor is decanted and the mud washed in a series of tanks so arranged that the wash water flows in the opposite direction to the mud, which is finally filter-pressed and thrown away.

The liquor is pumped to storage tanks and run by gravity to vessels heated by direct fire and the hot liquor pumped to vacuum evaporators. Each of these consists of a cone-shaped vessel with four 'calandrias' attached to it and a run-off pipe from the bottom of the vessel to a tank below. The calandrias are fitted with a number of tubes and the liquor is drawn through these tubes under vacuum while steam is passed into the calandrias. The liquor circulating through the tubes becomes concentrated and deposits in the vessel salt, which falls down the run-off pipe into the tank below, the pipe being sealed by the liquor in this tank, which automatically adjusts itself in depth to variations in the vacuum. The tank is fitted with an agitator, which carries the salt round to a boot, whence it is conveyed by a chain pump to a rotary crystalliser and thence to a centrifugal separator, from which a belt conveyor passes the finished salt to be bagged and shipped.

Potassium chloride from cement.—The recovery of potash as a by-product of the cement industry is described by Ross, Merz, and Wagner (U.S. Dept. of Agri. Bulletin, No. 572, 1917).

It has long been known that the potash content of the clays used in the manufacture of cement, varying from 1 p.c. to 4 p.c. as K_2O, can be volatilised into the furnace gases in the form of potassium chloride by the addition of sodium chloride to the mix in the kiln.

Several plants were erected in the U.S.A. during the Great War for the recovery of potassium chloride from cement kiln gases by the Cottrell system of electrical precipitation. The most successful of these installations appears to have been that of the Riverside Cement Works in California.

The problem is similar to that of the recovery of potash as a by-product of the manufacture of pig iron, except that as the gases from the cement kilns have already undergone combustion they are valueless, but the dust contains no impurities that are injurious to plant life, and can therefore be used for direct application to the land.

For this reason the recovery of potash-bearing dust as a by-product of the manufacture of cement in the form of a fertiliser should become practicable and commercially profitable as soon as plant is perfected for the recovery of dust from gases in the dry state, and, if so required, potassium chloride can be extracted from this dust by any simple method of lixiviation and crystallisation.

Potassium chloride from felspar.—Numerous papers have been published and patents taken out for the recovery of potash from felspar, which is a mineral common to most countries, containing from 5 to 10 p.c. of potash estimated as K_2O.

The methods suggested by various authorities differ only in detail, the principal being to fuse the felspar with sodium chloride.

Ashcroft (Eng. Pat. 119492, of 1917) suggests fusing the felspar with or without carbon or other reducing material, and treating with chlorine gas. Benham (Can. Chem. Jour. i. 1917) describes the treatment of felspar in a furnace with sodium chloride, the recovery of potassium chloride and the use of the fused material for the manufacture of drain pipes and similar crude pottery ware.

With regard to all these processes, it may be stated with some certainty that the fusing of felspar by any method for the recovery of potash cannot be operated successfully for commercial purposes unless accompanied by a profitable outlet for the solid residual, and there

is no evidence of any such outlet having yet been discovered.

Potassium chloride from beet-root vinasse.—This product, which always contains potassium sulphate and foreign salts, is described further on, under *Potash from beet-root vinasse.*

Potassium bromide KBr can be made in various ways, always starting from the bromine, obtained in America, in Scotland, or at Stassfurt. Only two or three processes have come into practical use.

The first consists in dissolving bromine in a solution of potassium hydroxide, which ought to be as pure as possible, evaporating the solution, ultimately with addition of a little charcoal, and igniting the mixture. At first the reaction is as follows: $6KOH+6Br=5KBr+KBrO_3+3H_2O$. On igniting, the charcoal reduces the bromate to bromide. The mass is dissolved in water, filtered, and the potassium bromide obtained by evaporation and crystallisation.

This process suffers from the drawback that the mass decrepitates strongly on drying, and further losses through volatilisation, &c., cannot be avoided. Hence another process is almost exclusively employed now, similar to that used for potassium iodide. An iron bromide is first prepared, and this is decomposed by potassium carbonate. Some iron bromide is obtained in the manufacture of bromine, the vapours being absorbed by metallic iron, but most of it is made by mixing bromine and iron in such proportions that the compound Fe_3Br_8 is obtained (*cf. Potassium iodide*). The solution of this bromide is filtered, and is run into a hot concentrated solution of potassium carbonate, until the reaction is exactly neutral or very faintly alkaline. 100 parts of iron bromide require from 56 to 60 parts of potassium carbonate, according to its purity. The solution is boiled for some time, to make the precipitate of hydrated iron oxides more dense; it is then separated from the latter by a filter or filter press, and is evaporated to dryness. The residue is dissolved again, leaving behind the difficultly soluble potassium sulphate, &c., and is evaporated for crystallisation. Up to sp.gr. 1·53 this can be done at a boiling heat; the further evaporation should be done at a gentle heat, as with the iodide, to obtain hard crystals. The crystallisation takes place in stoneware or enamelled iron dishes. The mother-liquor can be freed from carbonate by cautious neutralisation with hydrobromic acid, and from sulphate by means of barium bromide. Any chloride present cannot very well be removed from the bromide; hence the bromine employed should be as free from chlorine as is required. Iodide can be removed by boiling with bromine. The last mother-liquors are best used up for the recovery of bromine. The German Pharmacopœia permits the presence of 2 p.c. KCl and 0·1 p.c. K_2CO_3 in potassium bromide. The British Pharmacopœia specifies that when dried at 100° it shall contain not less than 98 p.c. of pure potassium bromide.

The drying of the potassium bromide takes place at 40° or 50°C., not above (to avoid decrepitation), on plates of stoneware or of sheet-iron covered with a very hard lacquer or with enamel.

The application of potassium bromide is mainly in medicine and photography.

Potassium iodide KI. There are many ways for preparing this salt, but only the following processes are used for manufacturing purposes.

1. *By means of potassium hydroxide.*—The reaction is, $6KOH+6I=5KI+KIO_3+3H_2O$. The potassium iodate on igniting yields up its oxygen and is converted into iodide, but as losses are caused by decrepitation and volatilisation, it is preferred to add some carbon in order to reduce the iodate.

The potassium hydroxide ought to be as pure as possible; most of the impurities of the commercial product would enter into the iodide, and could not be removed by crystallisation, owing to the great solubility of the iodide. Hence it is preferable to start with the purest procurable potassium carbonate such as is supplied in the crystallised form to flint-glass makers, or that made by calcining potassium bicarbonate. The carbonate is causticised in the usual manner, employing pure lime, and iodine is introduced in small quantities into the boiling liquor until it has been exactly neutralised. The solution is evaporated to dryness, adding to it in the syrupy state some lampblack or charcoal, previously treated with hydrochloric acid and thoroughly washed with water, to the amount of $\frac{1}{20}$ of the iodine present. The dry mass is gradually introduced into an iron pot, heated to redness, where it is brought to fusion, keeping the pot covered in order to prevent the iodide from volatilising. When completely fused, the mass is ladled out and is dissolved in water; the solution is filtered and is evaporated to about 1·82, when it crystallises on cooling. The evaporation is best performed by heating the solution in porcelain dishes on a sandbath, but not to boiling heat, the more concentrated liquors being farthest from the fire-end. A hood protects each dish from dust, draught, &c. In this way very good crystals are obtained.

The crystals, after draining, are dried on enamelled or lacquered iron plates in a current of hot air. If the salt is required to have an opaque appearance, the temperature is ultimately raised to 120° or 130°C.

2. *By means of iron.*—A solution of ferrous iodide is prepared by digesting 3 parts of iodine with 1 part of iron borings and about 8 of water. The solution is filtered and one-third of the original quantity of iodine is dissolved in it with the aid of heat, so that it now contains a ferroso-ferric iodide, Fe_3I_8. This solution is now mixed in a porcelain or enamelled iron vessel with a boiling solution of pure potassium carbonate, and the boiling is continued until the precipitate of ferroso-ferric oxide has become dense, whereupon it is separated from the solution of potassium iodide by filtration. The reaction is:

$$Fe_3I_8+4K_2CO_3=8KI+Fe_3O_4+4CO_2$$

The following modification, by Liebig, dispenses with the slow solution of iodine in ferrous iodide, and the troublesome frothing in the last reaction, owing to the escape of carbon dioxide. A solution is made of 12 parts iodine, 3 iron, and 32 water; to this is added, without previous filtration, a solution of 6 parts iodine in 12 parts caustic potash liquor of sp.gr. 1·345, and ultimately 9 parts of the same caustic liquor. The mixture is boiled for some time, filtered, evaporated to dryness, whereby a little ferric hydroxide

is separated, re-dissolved, filtered and brought to crystallisation as above. The product is extremely pure, free from iodate, and the yield almost theoretical.

3. *By means of cuprous iodide.*—Sometimes considerable quantities of cuprous iodide, containing from 60 to 66 p.c. of iodine, are shipped from Peru. This is converted into potassium iodide by washing it, suspending it in water acidified with a little sulphuric acid, passing in hydrogen sulphide until all the copper has been precipitated, adding enough solution of iodine in potassium iodide to destroy the excess of H_2S, separating the solution of hydriodic acid (containing a little finely-divided sulphur) from the precipitate, neutralising it with potassium bicarbonate, evaporating, separating the sulphur which has now become globular, and bringing to crystallisation.

Nearly all the potassium iodide manufactured is employed in medicine and for photographical purposes. For the former purpose it is required to be entirely free from chloride. The British Pharmacopœia requires that when dried at 100° it should contain not less than 99 p.c. of KI. Potassium iodide is occasionally largely adulterated with the cheaper potassium bromide.

Potassium sulphate K_2SO_4 is obtained as a by-product in several manufactures which are described elsewhere; thus, in the working up of beet-root vinasse (*cf. Potassium carbonate*), and in that of kelp, where it is separated as 'plate' sulphate,' containing from 76–83 p.c. K_2SO_4, with 9–21 p.c. Na_2SO_4, some KCl and other salts. It is also contained in the ashes of plants, and hence is present in commercial potashes; on purifying these it is obtained as a by-product, easily separable from the carbonate on account of the great difference in solubility.

The bulk of the potassium sulphate found in trade is, however, made either from kainite, or by the decomposition of potassium chloride with sulphuric acid.

Large quantities of potassium sulphate are found at Stassfurt and Kalusz, in the form of *kainite* $K_2SO_4,MgSO_4, MgCl_2,6H_2O$, always mixed with sodium chloride, calcium sulphate, &c., so that commercial kainite contains at most 70 p.c. of the pure mineral. A number of processes have been invented for preparing potassium sulphate, either from kainite or from mixtures of magnesium sulphate (in the shape of kieserite) and potassium chloride or carnallite. In most cases an intermediate product is made, the magnesium-potassium sulphate, $K_2SO_4,MgSO_4,6H_2O$, which occasionally occurs among the Stassfurt minerals, and has received the name of 'kalimagnesia' or 'artificial schoenite.' From this potassium sulphate is prepared with comparative facility, but at present it hardly pays to do so, at least in a sufficiently pure state for the manufacture of potassium carbonate; hence nearly all the latter is made from sulphate, obtained, with potassium chloride and sulphuric acid (*v. infra*), or from vinasse, while the schoenite is sold as a fertiliser.

1. *Preparation of artificial schoenite* (*kalimagnesia*) *from kainite.*—Borsche and Brünjes (D.R. PP. 10642, 10701, 11028, 12875, 17795) prepare a cold saturated solution of kainite and employ this for extracting fresh kainite at a temperature of 80°. The solution, which should have the sp.gr. 1·337, is clarified, and on cooling yields a crop of schoenite; the mother-liquors, which are rich in magnesium and sodium and potassium chloride, generally enter into the manufacture of potassium chloride from carnallite. This process is actually at work on a large scale.

Dupré and Hake (D. R. P. 6053) treat finely-ground kainite with a cold saturated solution of magnesium sulphate, at 20° or 25°C.; this carries away magnesium and sodium chloride, together with one-third of the potash, two-thirds of the latter remaining behind as schoenite. The dissolved 33 p.c. of potash is also partially recovered. This process is also at work, but not on a very large scale; the employment of magnesium sulphate makes it rather more expensive than the preceding one.

H. and R. Grüneberg (D. R. PP. 10754, 18947) extract the kainite by a hot solution of schoenite or of sodium chloride; on cooling schoenite crystallises out.

Precht (D. R. PP. 10637, 13421, 19456) treats kainite with water or previous liquors at 120°–145°, under a steam-pressure of 2–7 atmospheres, with mechanical stirring, in a very ingeniously-constructed apparatus, which permits a mechanical separation of the double salt formed from the solution and from the residual rock-salt. The double salt formed in this way has the formula $K_2SO_4,2MgSO_4,H_2O$, and is converted into schoenite by agitation with a small quantity of water. This process is also at work on a large scale.

Similar processes are those of Loefasz (D. R. P. 29223) and Nahnsen (D. R. PP. 10772, 24744).

Dupré (D. R. P. 53237) works up mixtures of kainite and sylvinite (75KCl+25NaCl) by treating them with a hot solution of kainite, when almost pure $K_2SO_4,MgSO_4,6H_2O$ crystallises out. The same inventor (D. R. P. 68572) passes ammonia gas into a solution of kainite, separates the precipitated $Mg(OH)_2$, and again treats with ammonia, whereupon the whole of the potassium, in the case of pure kainite, crystallises out as K_2SO_4, or, if NaCl is present, as pure potassium-sodium sulphate, $K_3Na(SO_4)_2$. The ammonia is recovered from the last liquor by treating it with the magnesia, previously obtained.

The Westeregeln Alkali Works (D. R. P. 50596) boil ground kainite with the last mother-liquor from the manufacture of potassium chloride, containing 30 p.c. $MgCl_2$, thus producing various salts.

The schoenite thus obtained, which is entirely used for agricultural purposes, has the following average composition:

Potassium sulphate . . .	48–52 p.c.
Magnesium sulphate . . .	32–36 ,,
Water	3–12 ,,
Sodium chloride . . .	1–5 ,,
Gypsum and insoluble matter .	0·2–5 ,,

Several processes for preparing schoenite from potassium chloride or carnallite and kieserite (Brünjes, D. R. P. 11; Ferber, D. R. P. 5068; Grüneberg, D. R. P. 5607; Westeregeln, D. R. P. 27404) need not be described here, because they do not seem to be profitable. The principal reaction taking place is

$$2MgSO_4+2KCl=K_2SO_4,MgSO_4+MgCl_2$$

or better

$$4MgSO_4+6KCl=2K_2SO_4,MgSO_4+2KCl,MgCl_2$$

Special processes for recovering schoenite from waste liquors are those of R. Grüneberg (D. R. P. 10753), Bernhardi (D. R. PP. 10821, 12493), Vorster and Grüneberg (D. R. P. 28772).

It is now a fixed rule of trade that 'crystallised' potassium-magnesium sulphate is to contain 41 or 42 p.c. and 'calcined,' 48 or 50 p.c. real potassium sulphate.

2. Kubierschky (D. R. P. appl. K. 29803) makes use of the fact that a solution of magnesium sulphate (kieserite), when appropriately diluted by water or KCl solution, on addition of solid KCl, at a temperature of 25°, does not yield schoenite, but at once gives a precipitate of potassium sulphate.

Saeger (D. R. P. 196500) describes a process for obtaining potassium sulphate from the mother-liquors of the manufacture of potassium chloride.

3. *Preparation of potassium sulphate from schoenite.*—This can be done by simply running a hot saturated solution of schoenite upon dry powdered potassium chloride. The reaction theoretically is :—

$$K_2SO_4,MgSO_4+3KCl=2K_2SO_4+KCl,MgCl_2$$

but practically twice the theoretical quantity of schoenite must be taken, half of which remains in solution. The potassium chloride is rapidly changed into sulphate, and this is separated from the liquor by centrifugal force, taking care that the temperature does not fall below 40°. Below this temperature, first potassium chloride, then schoenite, and at last carnallite, crystallise out. The reaction can also be brought about by digesting crystallised schoenite with a cold saturated solution of potassium chloride, best of all in a set of vessels methodically combined with one another (Precht, D. R. P. 14534).

Schoenite, or a mixture of potassium chloride and magnesium sulphate, can also be converted into potassium sulphate by heat. Superheated steam (Sprenger, D. R. P. 27965) acts only very partially, but the addition of carbon (in the shape of small coal, brown coal, &c.) causes the reaction to proceed to its end by somewhat complicated stages (Precht, D. R. P. 15747 ; Leopoldshaller Fabriken, D. R. P. 31148). Townsend (D. R. PP. 10641, 29307) heats a mixture of potassium chloride, magnesium sulphate, and aluminium silicate in a muffle furnace in the presence of steam. This method has been further worked out by the Ascherslebener Werk, in 1885, and seems to be successful. Hans Müller ignites the mixture of KCl and $MgSO_4$ with ferric oxide (D. R. P. 32325). Dupré and Hake produce, by means of lime or gypsum, a double sulphate of potassium and calcium, which is decomposed by igniting or by redissolving (D. R. P. 8021).

Nearly all the potassium sulphate made from schoenite, &c., is used for agricultural purposes.

In all processes for manufacturing potassium-magnesium sulphate (schoenite) or potassium sulphate, a great deal of trouble is caused by the large quantity of mother-liquor and the loss of potassium chloride from that cause. When this mother-liquor is boiled down, various salts are obtained which can be utilised as fertilisers. *Rubidium alum* is also obtained from such mother-liquors.

4. *Preparation of potassium sulphate by decomposing potassium chloride with sulphuric acid.*—This process, analogous to the first stage of the Leblanc soda process, was first carried out by Messrs. Vorster and Grüneberg in 1863, near Cologne, and in 1868 at Stassfurt. About the same time (1864–1869) it was introduced in North Germany, France, and England. This way of producing potassium sulphate is nearly always employed when the product has to be converted into carbonate.

The raw materials are (1) potassium chloride of high strength of either the Stassfurt or Alsace manufacture, or that from the working up of vinasse which already contains from 8 to 12 p.c. of sulphate, together with a little carbonate. Coarse-grained salt is preferred to muddy or lumpy salt. (2) Sulphuric acid of sp.gr. 1·67, generally made at the same works. This is a lower strength than that preferred for decomposing sodium chloride, where the reaction is not so violent.

The decomposition of potassium chloride is so closely akin to that of sodium chloride that we can refer in most respects to the article SODIUM.

The 'decomposing pans' (pots) are exactly similar to those used for common salt, so are the furnaces, of which all three descriptions, as employed for common salt, are in use here as well. But whilst in the case of sodium chloride the 'close,' or muffle furnaces are considered the best, owing to the better condensation of hydrochloric acid, many potash manufacturers prefer 'open'—that is, reverberatory—furnaces, a higher temperature being required for decomposing potassium sulphate and the work being done much more quickly (by one-third). Undoubtedly the best furnace for this work is Mactear's continuous revolving furnace as used at Kalk near Cologne.

The ordinary decomposing pans, which in England produce from 1500 to 2000 tons of salt cake before they are worn out, serve only for half or two-thirds that quantity with potassium chloride. At Stassfurt they employ thin pans, $2\frac{1}{2}$ ins. thick throughout, which last only for 250–500 tons of potassium sulphate. The charges are from 5 to 10 cwt. of potassium chloride, and the corresponding quantity of sulphuric acid, which must be varied according to the varying strength of the chloride. The chloride coming from the vinasse works contains carbonate, which must be taken into account. With muffle furnaces the work is considered sufficiently good if 1 to 2 p.c. KCl and 2 to 3 p.c. 'free' SO_3 is left in the sulphate. Each charge takes about an hour to finish.

With reverberatory furnaces the undecomposed KCl is only 0·5 to 1·5 p.c. ; the 'free' SO_3 1 to 2 p.c.

With Mactear's furnace the Kalk works produce from $22\frac{1}{2}$ to 25 tons of potassium sulphate in 24 hours ; the product contains only 0·7 to 1·0 p.c. KCl, and as much free SO_3 (that is, bisulphate). Theoretically 100 parts K_2SO_4 require 85·6 of pure KCl (corresponding to a yield of 116·8 of the former from 100 KCl), and 45·91 of SO_3=75·27 acid of sp.gr. 1·67 ; and the HCl escaping should be 41·84 parts=138 parts hydrochloric acid of $32\frac{1}{2}$ p.c. Practically with hand-furnaces 3·5 to 5 p.c., with mechanical furnaces 1 p.c., excess of sulphuric acid must be taken, or even more, if a minimum of undecomposed KCl has to be guaranteed.

The yield of sulphate is almost equal to theory, the small unavoidable loss being made up by matter mechanically taken up from the furnace, flue-dust, &c. The quality has been mentioned above.

The following is an analysis of good commercial sulphate made from 98 p.c. potassium chloride :

K_2SO_4	95·00 p.c.	SO_4H_2	1·84 p.c.
Na_2SO_4	0·50 ,,	CaO,Al_2O_3,Fe_2O_3	0·81 ,,
KCl	1·50 ,,	Insoluble	0·35 ,,

The yield of hydrochloric acid is usually only 70–75 p.c. of the theoretical one with reverberatory furnaces, 90 p.c. and upwards with muffle furnaces or the Jones and Walsh furnace, 95 p.c. with Mactear's continuous furnace.

The fuel used amounts to 9 cwt. of good Westphalian coal with muffle furnaces, or 4–5 cwt. coke and 3 cwt. coal for reverberatory furnaces. With Mactear furnaces there is no saving of fuel, since it is necessary to provide steam for the engine turning the furnace.

Potassium aluminium sulphate (*Potash alum*) (*cf.* ALUM).

Potassium carbonate. Impure potassium carbonate, commercial 'pot-ashes,' has been known from very ancient times. Aristotle mentions its preparation by the incineration of rushes, Dioscorides by that of argol. Kunckel, in the seventeenth century of our era, proved the identity of these two products. The Romans employed potashes in medicine and for soap-making; the latter is even now the most important outlet for that article, as soft soap cannot be made with soda. Otherwise soda tends more and more to displace the more expensive potash, and has done so in the manufacture of hard soap, in that of glass (partially even in that of flint glass and Bohemian crystal), and more recently, to some extent, even in some manufactures which formerly seemed to be only possible with the use of potash, as that of chromates, chlorates, and ferrocyanides. In the manufacture of oxalic acid from sawdust caustic potash is also considered indispensable.

Leaving aside such methods as cannot be classed among manufacturing processes (such as the incineration of argol or wine-lees) with or without potassium nitrate, we may enumerate the following commercial sources of potassium carbonate :—

1. *Mineral.*—(*a*) From potassium chloride and sulphate by Leblanc's or other processes.

(*b*) From felspar and other rocks containing potash.

(*c*) From blast-furnace gases.

2. *Vegetable.*—(*a*) From wood ashes.

(*b*) From beet-root molasses (vinasse).

(*c*) From kelp or varec (very unimportant).

3. *Animal.*—From the 'suint' of sheep's wool.

Potassium carbonate (or caustic potash) manufactured from the chloride or sulphate.—In 1861 Messrs. Vorster and Grüneberg, of Kalk, near Cologne, commenced working up potassium sulphate (which at that period was a by-product in working up vinasse cinder, less valuable than chloride, and difficult to get rid of) by the Leblanc process, and this industry has gradually spread over other parts of Germany, which is the principal seat of that industry. In England the Leblanc process seems to have been attempted with potash about 1863 or 1864, but it was only somewhat later employed for making commercial carbonate, and has not gained any great extension there. In France it was introduced in 1873, at Croix, near Lille, and at other works in the North.

We shall now enumerate the principal processes for manufacturing potassium carbonate from chloride or sulphate, omitting those which have been originally proposed for soda without special adaptation to potash.

(1) *From chloride, without passing through sulphate.*—The *ammonia* process, which is of such importance for the manufacture of soda, is not applicable to potash, because the solubility of potassium bicarbonate is too great. An attempt to overcome this by working in an alcoholic solution, by Grousilliers (D. R. P. 10552), was unsuccessful.

Ortlieb (D. R. PP. 5706, 9376, 13397), replaced ammonia by *trimethylamine*, which is obtained by a certain treatment of beet-root vinasse (*cf.* below). The great solubility of trimethylamine hydrochloride admits of separating the potassium bicarbonate; cold, pressure and agitation promote this object. The reaction is :—

$$KCl+N(CH_3)_3+CO_2+H_2O = KHCO_3+N(CH_3)_3,HCl$$

The limited supply of the reagent, its high price, its extremely unpleasant smell, are drawbacks to this process, which otherwise seems to have worked well in the experimental factory at Croix, where it was, however, given up after a short time.

Engel patented the following process (D. R. P. 15218) : Suspending *magnesia* or natural magnesite in a solution of potassium chloride, and passing in carbon dioxide under pressure, when a double carbonate of potassium and magnesium is precipitated, which can be decomposed into the single salts by heating or dissolving in water :

$$3MgCO_3+2KCl+CO_2+H_2O = 2MgCO_3,KHCO_3+MgCl_2$$

The recovery of magnesia from the chloride would have presented difficulties, but there must have been others as well, for the works started at Stassfurt were soon stopped. Delsol (D. R. P. 39903) patented an addition to Engel's process.

The magnesia-potash process has been worked out more successfully in another shape, principally by Precht, and is now carried out on a large scale. This process starts from the fact that trihydrated magnesium carbonate, treated with KCl and CO_2, forms $MgCl_2$ and solid sesquicarbonate, and that the latter can be transformed into solid magnesium carbonate and a solution of potassium carbonate. The first and principal part of the process is represented by the equation :

$$\underset{\text{Solid.}}{3(MgCO_3,3H_2O)}+\underset{\text{Liquid.}}{2KCl}+\underset{\text{Gas.}}{CO_2} \rightarrow \underset{\text{Solid.}}{2(MgCO_3,KHCO_3,4H_2O)}+\underset{\text{Liquid.}}{MgCl_2}$$

Lime-kiln gases (30–35 p.c. CO_2) are passed into a solution, saturated at 20°, of strong potassium chloride (95–97 p.c.), made into a paste with tri-hydrated magnesium carbonate with

application of a series of vessels and mechanical agitation. The solid double salt formed is separated by suction from the mother-liquor, and is washed with a solution of $MgCO_3$, until it contains no more than 0·1 or 0·2 p.c. Cl. The mother-liquor, containing a large quantity of $MgCO_3$ and KCl, is utilised in various ways. The solid potassium magnesium carbonate is treated principally by the D. R. P. 50786 of the Salzbergwerke Neu-Stassfurt, which consists in heating it under pressure in agitating boilers to 140°, which produces the reaction :

$$\underset{\text{Solid.}}{2(MgCO_3,KHCO_3,4H_2O)} = \underset{\text{Solid.}}{2MgCO_3} + \underset{\text{Liquid.}}{K_2CO_3} + 9H_2O + \underset{\text{Gas.}}{CO_2}$$

The $MgCO_3$ formed is anhydrous and reacts too slowly to be re-employed in the first stage ; it is either sold as such or converted into anhydrous MgO by calcining. Modifications are described in D. R. PP. 55182, 125987, 143408, 143595, 143409, 141408, 143594, 144742, 155007, 172313.

According to D. R. P. 143409, the potassium magnesium carbonate is decomposed by water at 80°, yielding K_2CO_3 and a crystalline form of $MgCO_3,3H_2O$, which is used over again.

A third process is described in D. R. P. 172313. The potassium-magnesium carbonate, stirred up in water, is decomposed at 40° by magnesia (hydrated or anhydrous), yielding solid $MgCO_3,3H_2O$ and a solution of K_2CO_3.

Sometimes the first process is combined with the second or third, commencing the decomposition by the latter and finishing it by the first. Another modification is described in D. R. P. 135329 of the Deutsche Solvaywerke, 157354, 188504.

In 1885, Borsche and Brünjes patented the production of carbonate from chloride or sulphate by means of ammonium-magnesium carbonate and carbon dioxide.

Wittjen and Cuno (D. R. P. 19197) employ zinc compounds in lieu of magnesium compounds for a similar process.

Scheele's process, treating an alkaline chloride with *litharge*, has been repeatedly attempted without practical success. It has been applied to potash by the Société anonyme Lorraine industrielle (D. R. P. 23701), and by D. C. Knab.

Gilchrist Thomas (D. R. P. 30209) treats alkaline chlorides in the shape of blocks in a heated converter with *pig iron*, containing little carbon, but upwards of 4 p.c. silicon, in a stream of hot air and superheated steam.

Wagner, in 1865, proposed precipitating potash by *hydrofluosilicic acid*, and decomposing the potassium fluosilicate by lime.

Several inventors utilise the slight solubility of potassium *bitartrate* (Goldenberg) and *binoxalate*. Bohlig decomposes the latter by magnesium carbonate. None of these processes is practicable.

The decomposition of alkaline chlorides by the *galvanic current* has been frequently attempted. This process has been applied to carnallite by Wellheim (D. R. P. 16126) at Aschersleben with machines of 120 h.p. The Griesheim Chemical Company at Frankfort have carried out the electrolytical manufacture of caustic potash and chlorine from strong potassium chloride on a large scale for some years past. It is also in operation at the Runcorn works of the Castner-Kellner Alkali Co., Ltd.

(2) *From sulphate.*—Leblanc's process will be described below. It has been extended to a direct treatment of *schoenite* by Vorster and Grüneberg, and Precht (in 1885) even patented a direct addition of magnesium sulphate to the potassium sulphate employed for that process. Clemm (1863) and Precht (1858) decompose schoenite by heating with *coal*, whereupon a mixture of magnesia and potassium sulphide is formed, which is treated with moist carbon dioxide.

Of the processes in which compounds of barium, strontium, aluminium, &c., also aluminium phosphate, are employed for decomposing alkaline sulphates, we mention only the process of Jannasch (D. R. P. 51224), in which potassium sulphate, obtained by a special process from kainite, is boiled with finely ground native barium carbonate (witherite). As the native mineral and no carbonic acid are employed, the decomposition is sure to be incomplete.

E. Pfeiffer states (Zeitsch. f. Chem. 8, 1338, 1375) that he decomposed, for some time, potassium sulphate with barium carbonate on a large scale. W. Bramley has patented the same process in a slightly modified form (Eng. Pat. 1050, 1886).

Dupré (D. R. P. 47037) mixes solutions, saturated at 0°, of equivalent quantities of potassium sulphate and sodium carbonate (containing 85 grams Na_2CO_3 and 139 grams K_2SO_4 per litre), and cools down very cautiously below 0°, passing a stream of CO_2 into the liquid ; or else 140 grams sodium bicarbonate +140 grams potassium sulphate, dissolved in 1 litre water, are cooled down to −6°, when 200 grams of Glauber's salts crystallise out, which are separated from the solution of potassium bicarbonate by a centrifugal machine. At −10° the separation of Glauber's salts is more complete, but then the process is interfered with by the formation of cryohydrates. A further patent (D. R. P. 52163) contains important improvements of the process.

Vogt and Figge (D. R. P. 31675) convert alkaline sulphates into a porous form by mixing them with silica, clay, magnesia, or lime, calcining, and moulding into small pieces. These are introduced into upright iron cylinders, in which the sulphate is first converted into sulphide by the action of carbon monoxide at a bright-red heat, carbon dioxide being given off, and then into carbonate by the action of carbon dioxide and steam at a lower temperature. These cylinders are combined to a set, into which carbon monoxide is passed at one end and hydrogen sulphide passes out at the other end. The cylinders are discharged from the bottom ; the mass is lixiviated, and the porous substance employed over again. This process does not seem to have been successful.

Kayser (U.S. Pat. 320256) converts alkaline sulphates into carbonates by a mixture of equal volumes of CO_2 and CO at a low red heat ; SO_2 escapes, and is utilised for converting chloride into sulphate.

Römer (D. R. PP. 66533, 67320, 67780) dissolves potassium sulphate (or schoenite) and potassium dichromate in water at 60° or 80° and

neutralises exactly with milk of lime, whereby the following reaction is produced :

$$K_2SO_4+K_2Cr_2O_7+Ca(OH)_2 = 2K_2CrO_4+CaSO_4+H_2O$$

The precipitated gypsum is removed by filtration, the remainder of it by precipitation with potassium carbonate, or by evaporation *in vacuô* at 80°. The solution of potassium chromate is concentrated by evaporation, cooled down and treated with CO_2, whereby potassium dichromate and bicarbonate are produced. The former crystallises out and $KHCO_3$ remains in solution. By boiling this down to 45°–50°Bé., CO_2 escapes and K_2CO_3 is obtained.

At the Buckau Chemical Works (Fischer's Jahresb. 1894, 469), kainite is treated with sulphuric acid, the escaping HCl being condensed. The solution is decomposed by milk of lime, separated from the gypsum formed and treated with barium sulphide. After removing the barium sulphate, the solution of sulphides is decomposed by carbon dioxide (converting the H_2S given off into sulphuric acid) ; the alkalis are converted into bicarbonates and the sodium bicarbonate crystallises out on cooling, leaving potassium bicarbonate in solution.

Potassium carbonate by the Leblanc process.

This process consists in fusing potassium sulphate with calcium carbonate and coal. Both the theory and the practical execution of this process are exactly similar to its original application to soda, *v.* SODIUM. This also holds good for the furnaces, lixiviating apparatus, boiling-down pans, &c. We shall here point out only those matters in which the potash process differs from the soda process.

The potassium sulphate is nearly always that obtained by decomposing potassium chloride with sulphuric acid. That obtained from schoenite is too light, and is easily carried away by the draught. Without damaging the process, some schoenite may be mixed with the K_2SO_4.

The furnaces are almost exactly like black-ash furnaces ; the only difference is that the hearth is made a little ' dished '—that is, with a depression of 2 ins. in the centre—to counteract the tendency of the melting mass to penetrate into the hearth and raise it up.

The usual mixture is : 100 potassium sulphate, 80 to 90 limestone, and 40 to 50 coal ; but on starting a new furnace the proportion of limestone and coal is somewhat increased until the furnace has attained its full heat. Small batches (of $2\frac{1}{2}$ to 3 cwt. sulphate) are finished in 40 to 50 minutes, large batches (up to 5 cwt. sulphate) in about 75 minutes, so that there is no advantage with the latter ; on the contrary, small batches are more easily worked, and the furnace suffers less ; there is also less volatilisation of potassium compounds. Usually thirty batches of 3 cwt., or thirty-five of $2\frac{1}{2}$ cwt., of sulphate are turned out in 24 hours.

Towards the end of the operation the fusing mass becomes thinner than with soda ; the end of the operation is at hand when the evolution of ' candles ' begins to diminish slightly, whereupon the batch must be drawn out at once. The temperature rises from 700° at the beginning to 900°C. at the end.

Good black ash from potash should contain 40 to 45 p.c. potassium carbonate (counting the hydroxide as such), and not above 0·5 to 1·5 undecomposed sulphate, and 0·5 to at most 1·0 sulphide. The less limestone and coal are used in the first stage the less caustic it contains. Cyanide is formed from the nitrogen of the coal, sometimes to such an extent that the recovery of ferrocyanide is a paying process. German coal yields less cyanide than English (Newcastle) coal.

100 parts of potassium sulphate, with an average proportion of limestone, yield from 157 to 163 parts of black ash.

The black ash is left to cool for 1 or 2 days, and is broken up in smaller pieces than with soda (say, not above 4 ins. diameter). The lixiviation takes place precisely as with soda. For each ton of black ash to be lixiviated in 24 hours there should be vat space amounting to from 250 to 350 cubic feet. The water is used in summer without heating ; in winter about 30°C. ; the ' strong vat ' should be about 40° to 45°C. The strong liquor, as it is run off, tests from 36° to 60°Tw. ; the average is 42°Tw. It is greenish-yellow, sometines with a reddish cast. It contains all the same impurities as soda tank-liquor. Pfeiffer quotes the following quantities found in two samples, calculated upon 100 parts of K_2CO_3 (+KOH) :

	a	*b*	
Potassium sulphate .	3·27	4·34	parts
,, sulphide .	3·17	2·35	,,
,, thiosulphate	1·72	3·61	,,
,, silicate .	1·98	2·24	,,
Total sulphur (as K_2SO_4)	9·6	11·36	,,

There is also aluminate, ferrocyanide, ferrosulphide, &c. The *tank-waste* ought not to contain above 0·2 to 0·3 p.c. of soluble potassium carbonate.

By directly evaporating the tank-liquor to dryness, and calcining, a yellow or reddish potash is obtained which must be purified by redissolving, bringing again to dryness, and calcining. It is decidedly preferable to *carbonate* the tank-liquors exactly as is done with soda liquors, whereby the hydroxide and sulphide are converted into carbonate, and the ferrous sulphide is precipitated. This can be done by gaseous carbon dioxide in the manner described for soda, or very advantageously by means of potassium bicarbonate.

The *evaporation* of the liquor takes place in pans heated by the waste heat of the black-ash furnace either from the top or the bottom. Pans fired from the top suffer less, and the evaporation takes place more quickly than with bottom heat, which requires about twice the heating surface ; still, bottom-fired pans are generally preferred in potash works, because the liquors are less contaminated with SO_2, soot, coal-ashes, &c.

The evaporation can be carried on with good liquors to 77°Tw. before any sulphate ' salts out.' At this point the liquor is run off into coolers, where most of the sulphate is precipitated in a muddy form, together with a little $K_2CO_3 2H_2O$. With inferior liquors, containing much sulphate, the sulphate may ' salt out ' even at 60°Tw., and this takes place in any case above 77°Tw. up to 123°Tw., at which point all the sulphate will

have been removed. That part which is precipitated in the pans during evaporation would, in bottom-fired pans, produce very inconvenient crusts unless it were constantly removed by 'fishing.' This can be done most conveniently with boat-pans or by Thelen's mechanical fishing-pans. In the case of top-fired pans such deposits are harmless, and hence at some works they employ bottom-heat up to 77°Tw., and top-heat above that point.

The potassium sulphate, precipitated both in the pans and by cooling the liquor, is drained, freed from adhering liquor by cold water, and used over again in the black-ash furnace; this is an advantage over the Leblanc soda process, where the sulphate remains with the soda-ash, and is thus lost. When using coal containing much nitrogen it pays to extract the potassium ferrocyanide, which is found together with the sulphate. The deposit is for this purpose dissolved by water and steam to sp.gr. 66½°Tw.; the solution is clarified and run into coolers, where the ferrocyanide crystallises out. It is purified by re-dissolving to 60°Tw. The yield is generally below 1 p.c. of the carbonate.

The *finishing operation* takes place in a calcining furnace, similar to those employed for soda, but always connected with a cast-iron pot or a wrought-iron pan, set at the end opposite the fireplace, for utilising the waste heat. In those pans the liquor is brought to at least 123°Tw., and sometimes to the state of paste. In the latter case the furnace-bed is made level; when intended for liquor of 123°Tw. it must be made to slope down from the working-door to a depth of 5 or 6 inches. In any case the furnace must be brought to a bright-red heat before charging it with fresh liquor or paste, so that a crust is formed at once on the bottom, and there is less tendency for the liquor to penetrate into the furnace-bed, which, of course, must be made with the greatest care, exactly like that of a black-ash furnace. The new crusts forming at the surface must be worked down, and when the whole mass is dry it must be detached from the brickwork and broken up by means of the 'rake' and the 'paddle.' In the intervals of working the mass the heat is raised by closing the door and stirring the fire until the surface shows just incipient fusion, but not above this point. When the mass has been brought to a red heat throughout, and into the state of a uniform powder, it is drawn out and is left to cool on an iron plate. With liquor of 123°Tw., four or five batches of 5 or 6 cwt. of potash can be turned out in 24 hours. It is important to avoid any interruptions of work, which nearly always produce cracks in the brickwork.

With carbonated liquors a single calcination furnishes a marketable product containing 85 to 92 p.c. carbonate, 10 to 2 sulphate, 2·5 to 0·5 chloride, and a little insoluble matter. This is, however, frequently *refined* by redissolving it with the aid of steam, in tanks provided with a suspended sieve or with a mechanical stirrer, to a strength of 110° or 112°Tw., and allowing it to settle, when, on cooling, most of the sulphate crystallises out. The clear liquor is further concentrated to 123°Tw. in the pans behind the calcining furnaces, and is calcined with special care. This refined product contains:

Potassium carbonate (hydroxide, silicate, aluminate)	from 92 to 98·5 p.c.
Sodium carbonate	„ 2·5 „ 0·5 „
Potassium chloride	„ 2·5 „ 0·6 „
Potassium sulphate	„ 3·0 „ 0·4 „

The quantity of silicate and aluminate is very slight. Phosphate, which always occurs in potash from vegetable sources, is absent here.

Hydrated potassium carbonate.—For some purposes, especially for flint-glass making, potash entirely free from sulphate, but containing 12 to 18 p.c. of water, is manufactured as follows: Ordinary carbonate is dissolved to a strength of 142°Tw., or even above this; the solution is allowed to cool and settle, which causes nearly all the sulphate to separate. The clear liquor is evaporated in flat-bottomed pans to the state of a thick paste; the fire is now drawn, and the mass is constantly stirred till it has been converted into a coarse powder. It is less deliquescent than calcined potashes; its composition approaches the formula $K_2CO_3,2H_2O$.

3. *Potash from felspar and other rocks.*—The recovery of potash from rocks containing it in large quantities (sometimes up to 14 p.c. K_2O), which undoubtedly by their decomposition have furnished all the potash existing in the soil, and hence indirectly that obtained from vegetable and animal sources, has been attempted by a number of chemists for many years past without much success. The process of Ward and Wynants consists in heating finely-ground felspar (orthoclase) with lime and fluorspar until the mass has fritted. On lixiviation potassium hydroxide and silicate are decomposed by means of carbon dioxide. The silica is precipitated, and potassium carbonate can be obtained from the solution in a very pure form. Both this and all similar processes are of little practical value, since the Stassfurt and Alsatian deposits have opened out an incomparably more convenient source of potash, sufficient for hundreds of years to come. The proposal of Spiller (J. Soc. Chem. Ind. 1882, 128), to heat felspar with calcium fluoride and sulphuric acid in order to obtain potassium and aluminium sulphate, has very little prospect of practical realisation.

E. Hart (U.S. Pat. 997671) prepares potassium sulphate from potassium-bearing rocks by fusing them with barium sulphide so as to give a glass, and extracting the potassium from the powdered product by a mineral acid. Potassium alum, for instance, is obtained by fusing 1 mol. orthoclase with 1 mol. barium sulphate and 2 at. coal and treating the product with sulphuric acid.

Thompson (U.S. Pat. 995105) mixes finely ground felspar with an alkaline acid sulphate and chlorides, say, 5 felspar, 5 acid sodium sulphate and 1·8 sodium chloride, keeps the mixture at a red heat for 2 or 3 hours, grinds it after cooling, lixiviates and allows the solution to crystallise. The acid sulphate, acting on the chlorides, liberates hydrogen chloride, which at the high temperatures acts upon the felspar with formation of potassium chloride; this, with the $NaHSO_4$, forms again HCl and K_2SO_4. In this way, he asserts, 80 to 90 p.c. of the potassium contained in felspar is recovered as sulphate.

Herstein (J. Ind. Eng. Chem. 1911, 426) fuses felspar with calcium chloride and a like quantity of calcium carbonate in revolving furnaces; potassium chloride escapes in the state of vapour, while cement clinker remains behind.

Potassium carbonate as a by-product of the manufacture of pig-iron and of ferrous alloys.—It has been shown (Chance, J. Soc. Chem. Ind. 1918, 37, 222) that by increasing the temperature of operating a blast furnace for the manufacture of pig-iron, provided that the ratio of base to silica is not too low, an increasing proportion of the potash contained in the ore as silicate is volatilised and may be recovered in the form of potassium carbonate from the furnace gases. In the manufacture of ordinary pig-iron the potash may be liberated more cheaply in the form of chloride by the addition of salt to the furnace charge. In the manufacture of ferrosilicon and other ferrous alloys, where the basicity of the charge is great and the temperature of operating necessarily high, practically the whole of the potash in the ores and coke is driven off as carbonate, sulphate, chloride, and cyanide with traces of sulphocyanide, &c. The carbonate largely predominates and its recovery presents no real difficulties. Perhaps the greatest of these is the recovery of the fume from the gas; this leaves the furnace at temperatures ranging from 500°C. up to 1000°C. and acts strongly upon steel at these temperatures. After cooling, the gas is washed with water and the potash salts recovered in solution or, preferably, it is passed through flannel or cotton fabric which retains the dust and fume. The dust is then lixiviated and treated with an iron salt to convert the cyanide into ferro-cyanide, and the solution is concentrated. This concentration may be made either in open pans and the less soluble impurities, sulphate, chloride, and ferrocyanide, salted out; or under vacuum in what is known as a "salting type" of vacuum evaporator. In either case the carbonate, being highly soluble, remains in strong solution together with the sulphocyanide while the less soluble salts are deposited. The carbonate solution is evaporated to dryness and furnaced with oxide of iron at a temperature above 300°C., when the sulphocyanide is destroyed and potassium carbonate is obtained of sufficient purity for commercial use. A purer potassium carbonate may be prepared by dissolving in water the commercial product and passing CO_2 gas into the strong solution when acid potassium carbonate is deposited in crystals. These crystals are dried and furnaced to convert them into the normal carbonate.

4. *Potash from wood-ashes.*—This was formerly the only source of potassium carbonate on a large scale. About the middle of the nineteenth century it lost much of its importance through the rise of the vinasse industry; and, since the manufacture of potassium carbonate by Leblanc's process has more and more extended, that made from wood-ashes has correspondingly receded into the background. Nor is this result very much to be deplored, for the ready sale formerly obtained for potash from wood-ashes led to the devastation of forests at an alarming rate. On the other hand, it is a fact that in some localities the only use to be made of timber is its conversion into ashes, and extraction of potash therefrom; but the places where this can be called in any way a rational process are getting more and more scarce. Several of the brands formerly found in trade have become extinct. Since the use of wood as fuel has also very much diminished during the last generation the collecting of ashes from this source, which were formerly sold to the potash manufacturers, is now too troublesome in most countries, and such wood-ashes are there only used for domestic and agricultural purposes. Only some parts of Russia, Transylvania, Illyria, Canada, and the United States, still continue to furnish supplies of commercial pot-ashes (pearl-ash, &c.).

Potash is an indispensable element for the growth of most plants, and hence is found in their ashes. But where it is associated with much silica and phosphoric acid the ashes contain but little carbonate, and are not available for the manufacture of potash. This, for instance, holds good of straw-ash. The only practically important source of potash is *wood-ash*; it is true that the ashes of several herbaceous plants contain a great deal more of potassium carbonate than the ordinary woods, and it has been actually proposed to grow such herbs for this manufacture; but this is irrational and without any hope of success, as these quick-growing plants exhaust the soil much more quickly than can be met by the natural decomposition of the minerals composing it.

The following table shows the percentage of total ash and of potash in some of the more important woods and plants:—

	Ash per cent.	Potash per cent.
Pine wood	0·34	0·045
Poplar wood	—	0·075
Beech wood	0·58	0·145
Beech bark	—	0·153
Ash wood	1 22	0·074
Oak wood	1·35	0·153
Oak bark	—	0·420
Box wood	—	0·226
Willow wood	2·80	0·285
Elm wood	2·55	0·390
Vines	3·40	0·550
Thistles	—	0·500
Rush	—	0·508
Ferns	3·64	0·626
Nettles	—	2·503
Vetch	—	2·750
Wormwood	—	7·300

In Canada most potash is made from elm, birch, larch, and maple.

The potash is contained in these plants in the shape of sulphate, chloride, silicate, and organic salts. The latter, on calcining, are converted into carbonate, part of which may be converted into hydroxide on lixiviation if lime is present; any silica present will pass into potassium silicate, and this renders the manufacture of potash from straw quite irrational. Where soda is present in large quantities the potash obtained must also be of inferior value. Hence the quality of potash found in trade is very varying, quite apart from actual falsifications with coal-ashes, soda, &c.

The manufacture of commercial potash is a

very crude process. The wood is burned in pits dug in the earth in places sheltered from wind. The collected ash (beech-wood ash is preferred to all other wood-ashes ; vine stalks, ferns, &c., where obtainable in quantity, are still better) is spread on a stone floor, sprinkled with water, and worked through until it is evenly damp. Sometimes (in Canada) a little lime is mixed with it, which afterwards causes the formation of caustic potash. The damp ash is placed in casks provided with a false bottom, covered with straw, and water (preferably hot) is poured over it. After some time the liquor thus formed is drawn off by a plug-hole at the bottom ; if it is about 32°Tw. strong it can be boiled down at once ; the weaker liquors and washings are used for lixiviating fresh ash. The residue, which with this rough style of working still contains much potash, is a good manure.

The boiling-down is also generally a very rough process. In lieu of pans possessing a large heating-surface (pans fired from the top would be the best) usually circular cast-iron pots fired from below are employed, in which the liquor is boiled down to dryness. In spite of stirring up the mass before it becomes quite dry much of it burns fast to the pot, causing a great waste of fuel and a speedy destruction of the pot. In America the mass is heated nearly to redness, and is converted into greyish-pink compact ' pot-ashes,' which are assorted into ' firsts,' ' seconds,' ' thirds,' and ' unbrandables.' The brown crude pot-ashes are calcined in reverberatory furnaces, which causes the carbonaceous and other organic matter to burn away, the hydroxide to be carbonated and the sulphide, &c., to be converted into sulphate. An excess of heat has to be avoided, because the mass would then fuse, and this would prevent the organic substance from being burned. The resulting product should be white or blueish—the latter from potassium manganate. A purer product is obtained by dissolving the product of calcination in water, separating the liquor from the insoluble substances, evaporating and calcining again ; the American ' pearl-ashes ' are thus made.

The common American ' pot-ashes ' are frequently made with addition of so much lime that they contain the major portion of the potash in the caustic state ; thus some of the silicate is also recovered which would be lost otherwise. This potash fuses below a red heat ; it is therefore only boiled down until the mass solidifies on cooling and appears in grey, red, or black lumps. This description of potash must be even more carefully protected against atmospheric moisture than ordinary commercial potassium carbonate, although this is also deliquescent. Such caustic potash is very much in request by soap makers ; it takes less lime in making their lye, and causes less loss, just in proportion to the smaller amount of lime-mud.

' Purified carbonate of potash ' is made from ordinary carbonate in two different ways. In one the carbonate is stirred up in an iron pot with 1½ or 2 times its weight of *cold* water, and the mixture which gets hot allowed to cool down before siphoning off the clear liquor. The sulphate and some chloride remain behind, together with the insoluble matter ; the residue is not washed (which would cause the sulphate to be re-dissolved), but only pressed. The liquor, containing mostly carbonate, but also chloride and silicate, is brought to dryness, stirring it up to the end. In the other the solution is made with *hot* water, the residue is exhausted in the same way, the liquors are boiled down to sp.gr. 1·50 and allowed to cool, when the sulphate and some chloride crystallise out. This process is more expensive than the former. In order to make still purer carbonate for flint-glass manufacture, pearl-ashes are calcined with a little sawdust, lixiviated, the clear liquor is boiled down and calcined, and this is repeated twice over ; the last product is dried down until it is converted into granular ' crystallised ' carbonate with 15 to 18 p.c. of water.

Another method of manufacturing purified carbonate of potash is to dissolve commercial carbonate of potash in hot water until the solution contains from 6½ to 8 lbs. of K_2CO_3 to the gallon. The solution is then allowed to settle and run off through a filter into carbonators where CO_2 gas under pressure is bubbled through the liquor. This is agitated by mechanical means and as it cools crystals of acid potassium carbonate are deposited until the cold solution is drawn off containing about 25 p.c. of acid potassium carbonate in solution. The crystals are then extracted and furnaced to drive off the CO_2, and normal potassium carbonate of considerable purity thus produced.

According to Chem. Zeit. Rep., 1908, 3, potashes are manufactured from the stems of sunflowers in 24 factories in Northern Caucasia, to the extent of 100,000 to 120,000 tons per annum.

The potash from bamboo-cane, made in British Burmah (Romanis, Chem. News, 45, 158), testing 32·54 K_2O, 0·98 Na_2O, 18·72 KCl, 16·95 SiO_2, 9·07 CO_2, 2·71 SO_3, 1·10 Al_2O_3 and Fe_2O_3, 19·43 H_2O, partakes more of the nature of a silicate than that of a carbonate (like all other potashes made from graminaceous plants).

5. *Potash from beet-root vinasse.*—In the last stage of the manufacture of sugar from beet-root a syrupy liquid is obtained, which, although containing a very large quantity of sugar, cannot be brought to crystallisation, owing partly to the presence of organic impurities, but chiefly to the large quantity of salts present. The latter circumstance prevents the utilisation of such ' beet-root molasses ' in a similar way to cane-sugar molasses. For a long time the only way of dealing with beet-root molasses was by diluting them with water, neutralising their alkaline reaction with sulphuric acid, causing the liquor to enter into alcoholic fermentation by means of yeast, and distilling off the spirit (which is of rather inferior quality). The liquor remaining behind in the stills, called ' vinasse ' in French or ' schlempe ' in German, was formerly always led back upon the fields on which the sugar-beet had been grown. To some extent this is still done ; nor can it be denied that this is, after all, the simplest and at the same time the most rational way of dealing with it, wherever carriage is practicable, for in this way the mineral substances (especially potash and phosphoric acid) taken from the soil in the shape of beet-root crops, are given back to it in a soluble form, together with the nitrates formed in the

plants, which are lost in every other process of utilising the vinasse.

On the other hand, the large quanity of potash contained in this liquor has, under ordinary circumstances, a greater commercial value, even deducting the expense of recovering it in the shape of potassium carbonate, than in that of dealing with molasses, whilst in Germany it has become more usual to extract the sugar by means of the osmose, the strontia, and the lime processes. The strontia process easily admits of recovering the potash in the shape of 'vinasse cinder'; but the dilute liquids, obtained by the osmose and the lime process, are usually only applied for manuring the fields. In France sometimes the osmose liquor is worked for potassium nitrate, which forms 50 p.c. of the 'salin' obtained by boiling down the liquor to 40°Bé. (Dingl. poly. J. 245, 192; 264, 510).

Sugar-beet may be said to yield about 1 p.c. of ash, nearly half of which consists of potash (calculated as K_2O), present in the juice to a great extent in the shape of nitrate and of salts of organic acids, all of which on calcining yield carbonate. Very little of it goes away with the sugar: nearly all remains in the molasses, which contain from 44 to 50 p.c. of sugar, 14 to 18 p.c. other organic substances, 16 to 18 p.c. salts, and 15 to 18 p.c. water; the ash amounts to 10 to 12 p.c. The ash, according to Krocker, is composed as follows,:

	Soluble	Insoluble
Potash . . .	47·88	1·70
Soda	2·34	0·17
Lime	—	5·08
Sodium chloride . .	12·92	—
Sulphur dioxide . .	1·53	—
Carbon dioxide . .	22·39	4·00
Silica	0·85	0·22
Phosphorus pentoxide .	—	0·29
Lime, magnesia, ferric oxide (as phosphates)	—	0·63
	87·91	12·09

of liquid manure. This was pointed out about 1830 by Dubrunfaut, to whom is due the introduction of the very important industry of beet-root potash, which, however, did not take firm root until about 1850, first in the north of France, and then in Belgium and Germany. In France this still forms the most usual way

Analyses of Commercial Potashes, Pearl-ashes, &c., from Wood.

Origin	Quality	K_2CO_3	KOH	Total available alkali calc. as K_2CO_3	Available potash calc. as K_2CO_3	Na_2CO_3	K_2SO_4	KCl	Analyst
American potash .	—	68·0	—	75·5	68·0	5·8	15·3	8·1	Pesier
,, ,,	1	41·7	49·6	108·2	106·4	1·4	4·0	2·0	F. Mayer
	2	19·4	44·4	87·8	77·2	8·2	16·1	5·6	
,, ,,	2	18·3	36·6	81·7	65·9	12·2	15·1	14·6	Grüneberg
	2	34·5	29·6	81·8	77·9	3·0	15·0	7·5	
Montreal potash	firsts	43·87–26·16	50·03–36·50	92·49–89·82	88·83–85·54	6·24–2·84	16·07–10·40	4·41–1·68	Tatlock
	seconds	38·53–21·71	42·44–30·63	85·79–85·08	76·24–73·98	11·47–8·52	18·92–9·18	12·82–6·13	
	thirds	46·31	6·14	72·10	53·86	17·81	20·53	7·63	
Canadian pearl-ashes	—	71·3	—	74·2	71·3	2·3	14·3	3·6	Pesier
,, ,,	—	65·0	—	70·2	65·0	4·0	21·0	7·0	Grüneberg
,, ,,	1	77·50	—	80·98	77·50	2·86	11·65	2·65	Tatlock
	—	71·38	—	74·53	71·38	2·31	14·38	3·64	
Tuscan potashes .	—	74·1	—	78·0	74·1	3·0	13·4	0·9	Pesier
,, ,, .	—	62·6	—	76·9	62·6	11·0	15·5	4·5	
Illyrian potashes .	1	89·3	—	89·3	89·3	0·0	1·2	9·5	Grüneberg
Hungarian ,, .	3	44·6	—	68·0	44·6	18·1	30·0	7·3	
Galician ,, .	—	46·9	—	51·6	46·9	3·6	29·9	11·1	
Russian ,, .	—	69·61	—	73·77	69·61	3·09	14·11	2·09	Pesier
,, ,, .	—	50·84	—	66·78	50·84	12·14	17·44	5·80	Bastelaer

Heidenpriem found in molasses ash:

	Soluble	Insoluble
Potash . . .	47·67	51·72 p.c.
Soda	8·00	11·43 ,,
Lime	3·12	5·04 ,,
Magnesia . . .	0·10	0·18 ,,
Carbon dioxide . .	27·94	28·90 ,,
SO_3,P_2O_5,SiO_2,Cl,Fe_2O_3	6·16	9·33 ,,

Manufacture of vinasse-cinder (*salin*, *schlempekohle*).—The vinasse, a liquid of about sp.gr. 1·028, and always of acid reaction (purposely brought about for the sake of fermentation, *v. supra*), is neutralised with lime, and is then concentrated by evaporation. Since the profitable working of this process depends entirely upon the economical evaporation of a dilute liquid, much ingenuity has been expended on the evaporating apparatus. The heat must act both as top and bottom heat, the flame travelling between two pans, or over the top of a pan covered with an arch, upon which another pan is set so as to be indirectly heated. The most successful and most widely-employed system for this purpose is Porions' furnace, in which the evaporating-surface is largely increased by splashing about the liquid in the fire gases by means of paddle-wheels revolving from 400 to 800 times per minute.

The heat required for evaporating the liquid is produced partly by an ordinary fire, partly by the combustion of the organic substance contained in the vinasse. When the latter has been brought to the syrupy state, say 60°Bé., it is transferred from the iron pan on to the bed of a reverberatory furnace, immediately attached to it, on which it is completely dried, whereupon it

takes fire and itself produces a large amount of heat. This is aided by the nitrates contained in the mass. The heat must, however, be so regulated that the mass is not brought to fusion; as when fused it would be difficult to lixiviate, and it would also contain lower oxidation-products of sulphur. The process is therefore finished when a carbonaceous mass has been formed, a sample of which yields with water on filtration a colourless solution. This is the 'salin brut' or 'schlempekohle' (vinasse cinder), a product which was formerly largely sold in this state, and employed chiefly for soft-soap and for the manufacture of saltpetre from Chilean sodium nitrate; it is now generally worked up into potassium carbonate and other salts.

The composition of vinasse cinder varies between very wide limits, according to the soil on which the beet had been grown. Grüneberg (Amtlicher Bericht über die Wiener Ausstellung, 1, 399) gives the following figures as the average composition of this product:

Potassium carbonate. .	30 to 35 p.c.
Sodium carbonate . .	18 to 20 ,,
Potassium chloride . .	18 to 22 ,,
Potassium sulphate . .	6 to 18 ,,
Insoluble (incl. carbon) .	28 to 15 ,,

but the analyses published by Sauerwein, Gohren, Kuhlmann, Esselens, Lefevre, and others, prove that the proportion of the ingredients may vary even more.

A large number of analyses of vinasse cinder are given by Hinz (Fischer's Jabresb. 1893, 389 *et seq.*).

In lieu of burning the syrupy vinasse on the hearth of an open surface, C. Vincent (Compt. rend. 84, 214) runs it, at a strength of 40°Bé., into iron retorts, and carbonises it with condensation of the formed vapours, the recovered liquids being subjected to a special treatment. This extremely ingenious process, by which trimethylamine and methyl chloride were for the first time obtained as commercial products, together with methyl alcohol and ammonia, was carried out on a large scale at Courriéres, in the north of France, but has not extended beyond there. A modification of Vincent's process was proposed by A. Zwillinger (D. R. P. 38419), who carbonises vinasse, brought to the syrupy state, in a retort by means of superheated steam.

The following description is an outline of Vincent's process. The cinder, obtained by heating the vinasse-residue in closed retorts, is very porous and easy to lixiviate; the potash made from it is very pure, and especially free from sulphate and sulphide. The gaseous products are submitted to a process of condensation similar to that usual at gasworks; a little tar and a considerable quantity of aqueous fluid is condensed, and much gas passes over, which may be used for heating purposes.

The aqueous liquid contains ammonium carbonate, hydrosulphide and cyanide, methyl sulphide, methyl alcohol, trimethylamine, and the volatile monobasic fatty acids. It is neutralised with hydrochloric acid, and the greater proportion of water is removed by distillation. The distillate contains, together with much water, methyl alcohol and methyl cyanide; by redistilling it with lime, the methyl alcohol can be set free, and calcium acetate remains behind. From 100 kilos. of molasses 1¼ litres of methyl alcohol is obtained. The original liquid, concentrated by distillation and allowed to cool, yields ammonium chloride (about 2 kilos. for 100 kilos. of molasses). The mother-liquor (about 1·8 kilos.) contains principally trimethylamine hydrochloride. It is further concentrated by evaporation, and the dry mass is subjected to prolonged heating. At 260° there begins a strong evolution of gases, and at 325° the decomposition is finished. The gases escaping consist of trimethylamine and methyl chloride, afterwards with much ammonia; they are passed through hydrochloric acid, which retains trimethylamine and ammonia, whilst methyl chloride passes on, is washed with water and collected in a gas-holder. The liquor is concentrated to a boiling-point of 140°C.; on cooling, nearly all the ammonium chloride crystallises out and trimethylamine hydrochloride remains in the mother-liquor. The gaseous methyl chloride is dried, and by means of compression and cooling is condensed to a liquid, boiling at −23°C., which is sent out in strong wrought-iron or copper drums, and used principally in the manufacture of aniline dyes and as a cooling agent.

The theory of the decomposition of the dry trimethylamine hydrochloride by heat is as follows. At first this salt is, like ammonium chloride, dissociated by heat, and much free trimethylamine is volatilised. The acid residue at a higher temperature undergoes the following reaction: $N(CH_3),3HCl=3CH_3Cl+NH_3$. This explains the final decomposition into trimethylamine, methyl chloride, and ammonia.

Elsewhere the recovery of methyl chloride and trimethylamine does not appear to have been attempted, but in several places the ammonia has been recovered by various methods. Thus Baswitz (Dingl. poly. J. 245, 415) runs the vinasse, concentrated to 31° or 41°Bé., in a thin jet into red-hot retorts. The gaseous products pass through a pipe filled with pieces of firebrick and heated outside by waste heat; further on some tar is condensed, rich in pyrrol and pyridine bases, then the ammonia is absorbed in sulphuric acid; finally the methyl alcohol is condensed by cooling, and the uncondensed gases are returned to the fire. Each retort takes a charge of 360 litres of concentrated vinasse every 12 hours; the produce of 4 retorts is: 87·5 kilos. ammonium sulphate, 30 kilos. liquor containing amines, 4 to 4·5 kilos. methyl alcohol, 57·5 kilos. tar. (The process did not pay when the prices of the above products went down.) H. Hirzel (Zeitsch. Chem. 11, 346) employs a vacuum apparatus with mechanical stirrer. Borsche and Sohn (Dingl. poly. J. 244, 85) carbonise the vinasse with lime in order to increase the yield of ammonia; they assert that up to 80 p.c. of the nitrogen can be thus obtained as NH_3. Similar processes are patented by E. Ernst (*ibid.* 244, 86; 245, 413), by Oppermann, by Gaillett, and by the Waghäusel Sugar Company (*ibid.*). Lederer and Gintl (*ibid.*) carbonise vinasse, or the liquors of the lime and osmose process in revolving drums by a continuous process, the gases being treated for the recovery of ammonia.

Other apparatus for treating vinasse are those of Kux (Ding. poly. J. 247, 163), of

Klauning (*ibid.* 261, 256), of Gontard (*ibid.* 258, 498), and of Theisen (*ibid.* 257, 405).

Working-up of the vinasse cinder.—The cinder is broken up into pieces of the size of a man's fist or rather less, and is methodically lixiviated with hot water in the usual way. The liquor is run off at a strength of 23–32°Tw. The black residue (grey after drying) contains from 8–12 p.c. of alkaline salts (partly potassium sulphate, partly insoluble in water), 20–40 p.c. carbonaceous matter, containing a little nitrogen, 15–30 p.c. calcium carbonate, and a few p.c. of other earthy matters. The first evaporation takes place by means of steam coils, and is carried to 74°–82°Tw., the concentration being higher in summer than in winter. Most of the potassium sulphate is now precipitated as a fine mud; after two hours' settling the clear liquor is allowed to cool down, when impure potassium chloride crystallises out. According to whether the salts are at once subjected to methodical washing or not, they contain less or more potassium carbonate, as shown by the analyses of Tissandier (Wagner Jahr. 1868, 286). The analysis of a large number of French samples of such chloride (by Blattner, unpublished) yielded—

Potassium chloride	66·21 to 87·55	p.c.
Potassium sulphate	5·27 „ 19·86	„
Potassium carbonate	0·10 „ 6·49	„
Sodium carbonate	0·40 „ 4·57	„
Water	1·40 „ 8·79	„

This product is principally employed for conversion into sulphate, and then into carbonate, by the Leblanc process.

The mother-liquor is further evaporated by open fire in wrought-iron pans with flat or saddle-shaped bottoms, in three stages, down to 127°–142°Tw. During evaporation, monohydrated sodium carbonate is separated, which must be fished out, and purified by washing and calcining; on cooling down, to 97°Tw., principally potassium chloride crystallises out. This is washed like that obtained previously, but beyond that strength the crystals consist principally of a potassium-sodium carbonate $K_2CO_3,Na_2CO_3,12H_2O$, together with some hydrated potassium carbonate, $K_2CO_3,2H_2O$. The double carbonate is re-dissolved in a little hot water and evaporated down to 127°Tw., during which operation nearly all the sodium carbonate separates as monohydrated salt, and is removed by fishing. The mother-liquor from this operation is boiled down, together with the mother-liquor formerly obtained, and is, after proper settling, calcined in a reverberatory furnace. It yields a crude potassium carbonate containing:

K_2CO_3	80–84	p.c.
Na_2CO_3	8–10	„
KCl	3–4	„
K_2SO_4	3–4	„
K_2SiO_3	0·25–0·5	„
K_2HPO_4	0·3–1·5	„
Insoluble	0·1–0·2	„

Bauer (D. R. P. 191105) obtains technically pure potassium carbonate from vinasse cinders by heating the solution to 53°Bé., separating the precipitated salts, heating the purified solution to 90°, until a concentration of 56°–62°Bé. is attained and allowing to cool, whereupon potassium sodium carbonate crystallises out and is decomposed into K_2CO_3 and Na_2CO_3 by fusing and keeping at 50°.

Part of the potassium sulphate is formed from thiocyanate; and this salt itself is partly formed during the evaporation from potassium ferrocyanide and sulphide as shown by the ferrous sulphide, always precipitated together with the fished-out soda. This purification from iron is very important, and is sometimes promoted by purposely adding potassium sulphide to the liquors in sufficient quantity to precipitate the iron. Otherwise, even white potash is discoloured on contact with the air. Once-calcined potash, when treated as above, is sufficiently pure and white, but otherwise it can be purified by re-dissolving, settling, and recalcining. The analyses given under the heading 'commercial vinasse potashes' show the character of different descriptions of this product.

6. *Potash from suint.*—The 'suint' or 'yolk,' which forms a third or more of the weight of raw sheeps' wool, was proved by Chevreul to contain, together with many other substances, a considerable quantity of potash, combined with fatty acids to form a soluble soap. Maumené and Rogelet were the first, in 1859, to utilise this for recovering potassium carbonate from the wool used at and near Rheims and Roubaix, and their example has been followed elsewhere, but not to any great extent. 100 parts of raw wool are stated by Maumené to yield from 14 to 18 parts of salts, or about 5 parts of potassium carbonate; hence the 60,000 tons of wool annually imported into the United Kingdom ought alone to yield about 3000 tons of potassium carbonate. Even at Roubaix, Rheims, and Elbeuf, in lieu of the 1200 tons obtainable from the wool consumed there, only 150 tons per annum are actually recovered; the total production of suint potashes in France, Belgium, and Germany probably does not exceed 2000 tons per annum. This is all the more to be regretted as the potash contained in suint in the ordinary course of washing raw wool in a running stream does not return to the soil, but merely contributes to the pollution of watercourses. But the difficulty in the way of the general adoption of the recovery process is, that it does not pay on the small scale, and that neither producers nor consumers of wool, in the majority of cases, will entrust the scouring of their wool to a central manufactory, where it is doubtful whether the different parcels can be kept entirely distinct. It is thus preferred by most wool-growers to wash their own wool, and, if possible, to bring the washings again upon their meadows.

The process for working the wool for suint potash is as follows. Instead of washing the raw wool first in a running stream, and afterwards scouring it with soap, soda, or putrefied urine, the wool is, before the proper scouring process, submitted to a methodical lixiviation with cold water, either in a series of casks or tanks, or in mechanically-acting washers, for instance that constructed by H. Fischer (Dingl. poly. J. 218, 484; 229, 446). The dilute washings are always utilised for the first treatment of a fresh quantity of wool. Thus a brown liquor of about sp.gr. 1·12 is obtained, which is evapor-

ated in iron pans of very different construction where the fuel can be efficiently utilised—for instance, in the reverberatory furnace of Werotte, in which the flame is drawn through the liquid itself by means of an exhauster; or by means of discs fixed on a shaft revolving in the boiling-down pan. It is important to concentrate the liquors by indirect heating either in open pans fired externally or by vacuum evaporation, as in the event of vapours of combustion containing sulphur being allowed to come in contact with the liquor, some of the carbonate is converted into sulphate. The difficulties of concentration by these means are considerable, owing to the frothing of the liquors, but they can be overcome. Thus a pasty mass is obtained, which is either calcined in an open furnace or submitted to destructive distillation in gas retorts, in order to recover ammonia and illuminating gas. The carbonaceous residue is lixiviated and the liquor is treated similarly to that obtained from vinasse cinder, producing, by fractional evaporation and crystallisation, successive crops of potassium sulphate and chloride. But as suint contains but little soda (in the case of inland-fed sheep only 2·3 Na_2O to 100 K_2O, with sheep fed on the sea-coast 13 Na_2O to 100 K_2O), the crystallisation of the double carbonate of potassium and sodium does not take place, the liquor being directly brought to dryness and calcined.

Analyses of Commercial Vinasse Potashes.

Origin	K_2CO_3	Na_2CO_3	K_2SO_4	KCl	Insol.	H_2O	Analyst
French potash	53·9	23·1	2·9	19·6	—	—	Pesier
Valenciennes potash	79·0	14·3	3·9	2·8	—	—	Grüneberg
Refined potash	92·68	3·98	0·43	2·45	0·06	0·50	Tatlock
,, ,,	91·22	2·89	2·76	1·92	0·08	0·85	,,
,, ,,	90·83	2·68	2·67	2·52	0·27	0·90	,,
,, ,,	90·25	2·52	3·81	2·92	0·21	0·45	,,
Belgium crude ash	43·0	17·0	4·7	18·0	—	—	Grüneberg
,, ,,	34·3	13·0	11·0	23·5	—	—	,,
Magdeburg crude ash	32·9	18·5	14·0	16·0	—	—	,,
,, ,,	27·1	18·0	10·0	9·5	—	—	,,
Wäghäusel (refined)	94·39	trace	0·28	2·41	0·18	—	v. Groningen
,, ,,	88·73	6·45	2·27	1·01	—	—	Keller
,, ,,	78·10	13·33	2·31	3·21	3·05	—	Tissandier
,, ,,	81·22	13·15	1·78	3·25	0·80	—	,,
,, ,,	91·25	4·73	0·80	2·61	0·61	—	,,

	From Verviers					First quality		Second quality
	Tissandier			Werotte		Tatlock		
K_2CO_3	71·52	79·01	72·25	68·50	64·30	91·20	89·41	80·57
Na_2CO_3	4·96	5·15	5·14	3·20	3·10	4·39	3·83	2·48
K_2SO_4	2·48	3·03	3·33	2·10	2·49	0·52	0·17	4·75
KCl	5·88	6·12	7·04	12·50	16·88	1·97	1·67	4·51
K_2SiO_3	—	—	—	8·50	8·00	—	—	—
Insoluble	11·98	5·28	11·19	1·48	1·55	0·04	0·06	0·30
Water	2·83	1·20	1·05	2·77	2·80	1·60	4·70	7·25

The following analyses, by W. Graff, give the composition of wool potash, made in Germany—viz. (*a*) by the simple steeping process, (*b*) and (*c*) by methodical lixiviation :—

	a	*b*	*c*
K_2CO_3	31·16	75·01	71·40
K_2SiO_3	17·44	0·62 }	1·50
K_2HPO_4	0·50	0·71 }	
K_2SO_4	2·00	4·12	5·32
KCl	3·93	5·68	6·74
Na_2CO_3	3·15	3·07	4·55
H_2O	1·22	1·30	4·72
Insoluble	40·60	9·49	5·77

Potassium hydroxide (*Caustic potash*). The majority of soap-makers prefer causticising their own potassium carbonate, as they mostly do not require to do this thoroughly. Still the manufacture of caustic potash in the solid state is carried on to some extent on the large scale, with black-ash made by the Leblanc process from potassium sulphate, precisely in the same manner as caustic soda is made, so that we can refer to that article. In this place we need only give the analyses (by Tatlock) of some

samples of caustic potash made on the large scale :—

—	White	Brown or cream	
Potassium hydroxide .	77·64	75·64	74·05
Potassium carbonate .	4·62	2·54	3·14
Potassium sulphate . .	0·38	0·21	0·69
Potassium chloride . .	2·29	0·93	2·26
Potassium nitrite . .	0·87	—	—
Sodium hydroxide . .	4·67	2·59	3·20
Soluble silica and alumina	0·30	0·20	0·55
Insoluble matter . .	0·02	0·22	0·69
Water	8·84	17·80	15·80
Available potash, K_2O .	68·33	65·24	64·31
Available alkali, calculated as K_2O . .	73·83	68·28	68·08

For a mathematical investigation of the reaction between potassium carbonate and calcium hydroxide, *see* Belloni (Ann. Chim. Applicata, 1918, 9, 115 ; J. Soc. Chem. Ind. 368 A).

Graff (D. R. P. 88003) prepares potassium hydroxide from vinasse cinder. The solution of this product is causticised, concentrated by evaporation, separated from the potassium sulphate and chloride which crystallises the solution now containing only sodium and potassium hydroxides. The necessary quantity of potassium carbonate is added to convert the sodium present into the double salt $KNaCO_3$, which is removed by concentration and cooling, leaving pure KOH in solution. Or else the potassium hydroxide is separated from the potassium-sodium carbonate by evaporating the mixture to dryness and extracting the KOH by means of alcohol.

N. T. Bacon (D. R. P. 99344) employs a hot, concentrated solution of strontia into which solid potassium carbonate is introduced. The conversion into KOH and $SrCO_3$ is almost instantaneous.

The Chemische Fabrik Griesheim (D. R. P. 108500) gives detailed prescriptions for the purification of caustic potash solution by diffusion. The Salzbergwerk Neustassfurt (D. R. P. 117748) effect such a purification by fractionated crystallisation at 60°.

I. A. Reich (D. R. P. 161795) prepares caustic potash by boiling potassium silicofluoride with caustic lime.

Crystallised potassium hydroxide is obtained by Salzbergwerk Neustassfurt (D. R. P. 18935) by conducting the concentration of the solution in a special manner.

Potassium silicate. Potassium silicate, or soluble potash glass, has approximately the formula $K_2O,4SiO_2$. It is prepared by fluxing together white sand and potassium carbonate in a reverberatory furnace, preferably with a little charcoal, which aids in expelling the carbon dioxide by reducing it to monoxide. The following proportions are stated by N. Fuchs to be suitable : white quartz sand 45 parts, commercial potashes 30 parts, wood charcoal 3 parts, to be fused for 5 or 6 hours until no more gas escapes ; the product is 58 parts of silicate. O. Schür prescribes : 90 sand, 62·5 potashes, 1·5 charcoal ; product 112·5 to 115 soluble glass. Some manufacturers employ potassium sulphate in lieu of carbonate, together with a larger proportion of charcoal, but this process is much more difficult than with carbonate. Solid potassium silicate is a transparent glass, tinged a bluish-green, which is either sold as such, or in the state of a thick solution, produced by boiling it with water for a long time, preferably under pressure. Frequently a mixed silicate of soda and potash is produced, either by using a mixture of potash and soda in the fluxing process, or by mixing the solutions.

Potassium silicate can be obtained also by dissolving very finely divided silica (in the shape of ignited and ground flints, or of kieselguhr, or Farnham stone) in a very strong solution of caustic potash, by prolonged boiling, or in a shorter time by boiling under pressure. An analogous process is actually used for the manufacture of sodium silicate.

The following analyses, by Tatlock, show the composition of commercial potassium silicate :—

—	Solid			Liquid	
	a	*b*	*c*	*d*	*e*
Potash (as silicate) . . .	23·54	22·91	9·46	4·31	3·49
Soda (ditto)	1·28	1·28	1·52	4·20	1·80
Silica	65·60	66·84	23·28	24·32	16·64
Potassium sulphate . . .	0·87	1·08	0·67	0·61	1·48
Potassium chloride . . .	0·48	0·48	0·41	0·67	3·52
Alumina and ferric oxide . .	0·40	0·32	—	—	—
Water	7·83	7·09	64·66	65·89	73·07

The total quantity of potassium silicate manufactured is but small in comparison with that of sodium silicate ; for mixing with soap it can be nearly always replaced by the cheaper sodium silicate. It is, however, used in fresco painting, and for a few other purposes.

Potassium nitrate (*Saltpetre, nitre*). Potassium nitrate KNO_3 is first mentioned by Geber, in the eighth century, and again by the alchemists of the thirteenth century. Agricola in 1546 gives a description of its manufacture from saltpetre earth, which does not materially differ from the present process. The artificial preparation of this substance from Chilean sodium nitrate was due in the first instance to the greatly-increased demand produced by the

Crimean war, and has gained very large dimensions, being now much more important than the working of natural saltpetre earths.

I. *Manufacture of saltpetre from natural saltpetre earths.*—Such earths are found principally in East India, where the district of Tirhût, in Bengal, is the most important one in this respect, and whence nearly all the natural saltpetre still manufactured is derived. Smaller deposits are found in Egypt, Persia, Hungary, Apulia, Kentucky, &c., none of which is of more than local importance.

The raw material occurs only occasionally in real strata or nests; it is mostly a product, continually re-formed by the action of atmospheric air upon nitrogenous organic matter in the presence of bases, such as lime, magnesia, and potash (for which, in Peru, near the sea-coast, soda is substituted). The organic nitrogen is not simply oxidised by atmospheric oxygen; the process of 'nitrification' never takes place except in the presence of certain bacteria, as first proved by Schlösing and Müntz (Compt. rend. 84, 602; 85, 1018; 86, 892), and confirmed by many subsequent observers.

Whether the formation of ammonia is an indispensable intermediate link remains an open question. The nitrification process is, of course, much more intense in hot countries, where it is promoted by the abundance of organic matter, and by the moist and warm atmosphere. It is always dependent upon a supply of nitrogenous organic substances, and has nothing to do with the direct formation of nitric acid from atmospheric oxygen and nitrogen by the electric discharge. Saltpetre earth is, consequently, chiefly found in the neighbourhood of villages, where urine, &c., yields an abundant supply of organic nitrogen. In Bengal it is collected by a special caste, the 'Sorawallahs,' partly from the soil, partly from the surface of mud heaps, mud cottages, &c., by scraping off the uppermost layers which show a white efflorescence.

The following analyses show the composition of some Indian saltpetre earths:—

—	Tirhût (Stevenson)	Tirhût (J. Davy)	Ceylon (J. Davy)
Potassium nitrate .	0·7	8·3	2·4
Calcium nitrate .	0·9	3·7	—
Magnesium nitrate .	—	—	0·7
Sodium sulphate .	2·7	—	—
Sodium chloride .	1·4	0·2	—
Calcium sulphate .	—	0·8	—
Magnesium sulphate .	—	—	0·2
Calcium carbonate .	44·3	35·0	26·5
Insoluble in acids .	50·0	40·0	60·8
Water and organic substances .	—	12·0	9·4

Ganges mud, according to Warneford Lock, contains 8·3 p.c. potassium nitrate, and 3·7 p.c. calcium nitrate. This earth is lixiviated in earthenware dishes, or wooden boxes, or in pits dug in the ground and made tight by a clay puddle. The liquor is concentrated in iron pots, or sometimes only by solar heat, and a crop of very crude saltpetre is thus obtained. The mother-liquor is further evaporated to obtain common salt, and the last mother-liquor, which contains a large quantity of calcium and magnesium nitrates is mostly run to waste. Occasionally a somewhat more rational process is pursued, by mixing wood-ashes with the saltpetre earth previous to lixiviation, or adding such ash to the solution during concentration; the potassium carbonate of the wood-ash then converts the earthy nitrates into potassium nitrate. The crude saltpetre, obtained from the clarified liquor by slow evaportion in earthenware pots, is called 'dhouah'; it contains from 45 to 70 p.c. KNO_3, and is re-crystallised by native merchants, who sell it in this state as 'kalmee.' The following analyses, by Tatlock, show the composition of some samples of Indian saltpetre:—

—	Bengal ordinary 1	Commercial 2	Bombay 1	Crude 2
Potassium nitrate . . .	96·51	89·36	72·46	36·06
Potassium sulphate . . .	0·89	0·75	0·13	2·64
Potassium chloride . . .	0·84	4·57	6·65	—
Sodium nitrate	—	—	—	0·26
Sodium chloride	0·20	0·31	17·41	47·43
Calcium sulphate . . .	—	—	0·19	2·21
Magnesium nitrate . . .	—	1·97	0·17	2·08
Insoluble	0·21	0·14	0·14	1·55
Water	1·35	2·90	2·85	7·95

A sample of the 'refuse salt' left behind on recrystallising the first crop of crude saltpetre, contained 8·83 K_2SO_4, 13·15 KNO_3, 21·14 KCl.

According to Ljubawin (Fischer's Jahresb. 1885, 262), there is a large deposit of saltpetre earth in the Khanat of Khiva, south-west of Fort Nukus, of the following composition:—

Soluble in water . .	27·89 p.c.
Soluble in hydrochloric acid	17·14 ,,
Carbon dioxide . . .	5·73 ,,
Insoluble in acids . .	48·42 ,,
	99·18 ,,

The portion soluble in water contains:—

KNO_3 .	5·52 p.c.	$CaSO_4$.	3·25 p.c.
$NaNO_3$.	4·05 ,,	$MgSO_4$.	0·66 ,,
$Mg(NO_3)_2$	1·04 ,,	Total nitrates	10·61 ,,
NaCl .	12·90 ,,		

Saltpetre earths are found, and are worked by processes quite similar to those used in India, in some places in Persia, Egypt, Spain, Hungary (near Debreczin) and elsewhere.

An *artificial saltpetre earth* is, or formerly was, prepared in some European countries (Hungary, Switzerland, Sweden) by mixing a

porous soil containing much calcium carbonate, with decaying animal substances; for instance, by preparing such a soil underneath the floor of stables where cattle and sheep are kept, the urine penetrates into the soil, and there undergoes the nitrification process. In Sweden, where formerly every landowner was obliged to furnish to Government a certain quanity of home-made saltpetre, all sorts of animal refuse were used in this manner, in special 'saltpetre plantations.' About 100 tons per annum were made in Sweden in this way, but this process has been given up as unprofitable. In France, during the wars of the Revolution, when Indian saltpetre was unobtainable, that process was made compulsory by a decree of the Convention, and it is asserted that 2000 tons per annum were then made in this way; but there also the home manufacture had to be given up as soon as saltpetre could be imported from the East. Since the manufacture of saltpetre from nitrate of soda is making a severe competition even to Indian saltpetre, it seems quite hopeless to look to European sources for that substance; here the nitrogenous substances are better utilised for agricultural purposes.

Another kind of crude saltpetre, made from the mother-liquors from the working of 'caliche' for sodium nitrate, is sometimes sent to Europe from South America. It contains from 16 to 26 p.c. of potassium nitrate, 51 to 77 p.c. of sodium nitrate, 1 to 3 (exceptionally 16) p.c. of sodium chloride, and small quantities of sulphates and iodates. Its value is hardly greater than that of its equivalent of ordinary commercial sodium nitrate.

According to Sacc (Compt. rend. 99, 84), in Bolivia, near the village of Aranè, East of Cochabamba, a large deposit has been found of the following average composition: 60·7 potassium nitrate, 30·7 borax, traces of common salt, and water, 8·6 organic matter. If this were confirmed, it would be very valuable indeed.

Refining of saltpetre.—The East Indian saltpetre, before it can be used for the manufacture of gunpowder or other purposes, must be purified, especially from chlorides. This is done on a very large scale in England, France, and Germany (especially at Hamburg). The most usual is the French method. In an iron or copper pan 1050 kilos. saltpetre is dissolved in 600 litres of water at a gentle heat; the solution is brought to boiling heat, and another 1800 kilos. of saltpetre is dissolved in it. When employing these proportions with saltpetre containing about 20 p.c. of chlorides, the nitrate is dissolved completely, the chlorides but partially. The latter are fished out with a perforated ladle. If calcium or magnesium salts are present, potassium carbonate is added until a fairly alkaline reaction has been produced. The hot clear liquor is diluted with 300 litres of water, a solution of 1 kilo. glue in 20 litres of hot water is stirred into it, and the whole brought to boiling again. The glue combines with the organic substances present forming a scum, which rises to the surface and is carefully removed. When no more scum rises to the surface, the liquor is allowed to settle for 24 hours, preventing any cooling down below 90°C., and the clear portion is run into flat copper coolers. As soon as the crystallisation begins, the liquid is constantly stirred, either by hand or better by machinery. Thus the potassium nitrate separates as minute, floury, crystals, which do not, like large crystals, enclose mother-liquor in hollow spaces. The crystal flour is drained; the mother-liquor (500 to 600 kilos.) is used over again in dissolving fresh saltpetre.

The small crystals must now be washed to remove all adhering mother-liquor. This is done in vessels provided with a perforated false bottom, covered with linen. When all liquor has drained off, the bottom tap is closed, cold water is sprinkled upon the salt by means of a rose, the whole is allowed to stand for some hours, and only then is the liquor run off. This is repeated several times, until the liquor shows next to no reaction for chlorides. The last liquors are used in a new operation for the first washings. In this way the chlorides may be brought down to 0·005 p.c.

The drained crystal flour is dried in stoves or frames covered with canvas, or better on steam-heated pans, with mechanical stirring (just as they have been described for potassium chloride), and is mostly sold in this shape. Sometimes it is required in the shape of large crystals, which are very easily obtained by dissolving the flour in a small quantity of hot water and allowing the liquor to cool quietly and slowly. Exceptionally, it is fused into cakes or drops, which always contain a little nitrite (the 'sal prunellæ' or 'nitrum tabulatum' of pharmaceutical chemists).

II. *Manufacture of potassium nitrate from nitrate sodium.*—'Artificial saltpetre' was first made on a small scale by Longchamps and Anthon, with the aid of Chilean sodium nitrate and of potassium chloride, which, however, at that time was only obtainable from kelp, and was too expensive. When, in consequence of the increased demand for saltpetre during the Crimean war, especially in Russia, the manufacture of that substance from Chilean sodium nitrate became more remunerative, it was first carried out, in 1853, by Nöller, Grüneberg, and others, with the aid of caustic potash and of Russian potassium carbonate; later on, more cheaply, with that of *vinasse cinder* ('schlempekohle' recovery of nitrate of potash from Chile nitre), which was used directly, without any separation of the salts. For this purpose sodium nitrate and a corresponding quantity of vinasse cinder were dissolved at the same time in boiling water; by the reaction $K_2CO_3+2NaNO_3=2KNO_3+Na_2CO_3$ anhydrous sodium carbonate was produced, which was fished out of the boiling liquid, together with the sodium carbonate originally present, and with the less soluble potassium salts, while the potassium nitrate remained dissolved at boiling heat and only crystallised out on cooling. The mother-liquor yields a mixture of about 53 parts NaCl, 31 Na_2CO_3, and 10 K_2SO_3, which was used by soap-makers (*cf.* Dingl. poly. J. 118, 200; 155, 418; 163, 314; 166, 75; Chem. Zentr. 1872, 491). This process has been given up long ago, principally because the separation of the salts is too difficult and the value of potassium carbonate is too great.

The separation of the substances is easier when *caustic potash* is employed, in which case the reaction produces potassium nitrate and

caustic soda; the mixture can then be allowed to cool. The potassium nitrate is all but completely separated as fine crystals, and sodium hydroxide, with some impurities, remains in solution. By further concentration solid caustic soda can be obtained. This process was carried out by Nöllner, Landmann, and Schnitzer (Dingl. poly. J. 117, 68; 162, 132) by adding lime to the boiling mixture of potassium carbonate and sodium nitrate until the alkali was causticised, whereupon the liquid was separated from the lime-mud, concentrated by evaporation, and allowed to crystallise. Much more rational than this was the process carried out at St. Helens in 1864 (*ibid.* 182, 385), decomposing potassium chloride by sulphuric acid, converting the potassium sulphate by Leblanc's process into a kind of black-ash, dissolving and causticising the caustic solution to sp.gr. 1·50, adding an equivalent quantity of sodium nitrate and allowing the potassium nitrate to crystallise by cooling. The mother-liquor was further concentrated, during which operation some salts were separated and fished out, and on cooling yielded a second crop of potassium nitrate; the second mother-liquor was worked up as caustic soda. This process does not seem to be worked now.

The process of Bolley (Wagner's J. 1860, 201; 1866, 22), converting sodium nitrate by means of barium chloride into barium nitrate, and converting this by potassium sulphate into barium sulphate ('permanent white') and potassium sulphate, is evidently not fit for general use, and can only pay in very exceptional circumstances.

The only process now in practical use is that of employing *potassium chloride*, originally proposed by Longchamps, and worked out by Anthon (since 1840, but more especially in 1858, Dingl. poly. J. 149, 39) in the shape in which it is now carried out. A theoretical study of the conditions of equilibrium between the reciprocal pairs of salts: KCl, $NaNO_3$ and NaCl, KNO_3, has been made by Meyerhoffer (Ber. 1904, 261, *et seq.*). The technical forms of the process have been described by Lunge (Dingl. poly. J. 182, 385) and Pick (*ibid.* 215, 222), and it is carried out in several modifications, the best of which will now be described.

Stassfurt 'muriate of potash,' containing not less than 80 p.c. KCl, and commercial sodium nitrate (95 p.c.), are brought together with mother-liquors from a previous operation and with the liquid obtained by washing the nitre bags. (The washed nitre bags, when dry, are exceedingly easily inflammable, and must be treated with the necessary caution.) The operation is performed in covered wrought-iron cylinders, 8 ft. diameter and 6½ ft. high, provided with a mechanical stirrer, a steam coil, and a tap for an open jet of steam; also with a 6-inch pipe in the cover, through which the steam given off in the cylinder is passed under the double bottom of the mother-liquor tank. The liquor is first concentrated by means of the steam coil to sp.gr. 1·53, adding a little oil in case of frothing, whereupon the materials are charged through the man-hole, first 3 or 3½ tons of sodium nitrate, then the corresponding quantity of potassium chloride, which is so calculated that a very slight excess of nitrate is present. The whole is boiled for half an hour to complete the decomposition, and is then run through a 4-inch tap on to the filter or strainer, consisting of a tank 8 by 8 by 5 feet, with a canvas-covered false bottom at a height of 4 ins. above the true bottom, and a steam-pipe between the two for keeping the liquor hot. Here the sodium chloride formed in the reaction

$$NaNO_3 + KCl = KNO_3 + NaCl$$

which, owing to its relatively slight solubility in the hot concentrated solution, has been almost entirely precipitated in the solid form, is retained on the filter, while a liquor of sp.gr. 1·63 and a temperature of 95°C. runs off into the coolers. The common salt left on the filter is covered with hot mother-liquor, which is run off at a strength of 1·50 to 1·53, also into the coolers. The washing is then continued with liquors of decreasing strength, ultimately with pure water, until the salt contains only 0·6 to 0·9 p.c. of nitrate; at some works they go down to 0·25 p.c. The coolers are shallow iron vessels provided with either oscillating or revolving agitators, which can be lifted out of the liquid. The liquor is kept in agitation during the whole time of cooling, which, with a depth of 8 ins. in the vessels, ought to be finished in 30 to 36 hours. Sometimes this is hastened by a stream of water circulating on the outside of the vessel.

The mother-liquor, of sp.gr. 1·345–1·357, is run off into tanks provided with a double bottom, where it is heated by waste steam in order to be used over again at the first operation. 100 parts by volume of such mother-liquors contain:

	a	*b*	*c*
Potassium nitrate .	29·40	25·5	26·4
Sodium chloride .	25·72	14·2	17·18
Sodium sulphate .	1·32	1·06	1·81
Magnesium chloride.	2·10	6·2	8·19
Sodium nitrate .	—	19·6	7·19
Sodium iodide .	—	—	0·76

(*a*, sp.gr. 1·348 at 19°; *b*, sp.gr. 1·395 at 17·5°; *c*, remaining after working up 5000 tons of Chilean nitre).

The crude saltpetre flour, containing 7–9 p.c. NaCl, and 0·5–0·7 p.c. $MgCl_2$, is drained on one side of the cooler, and is washed with the liquor resulting from the washing of the refined saltpetre, with the use of the agitating gear, until the chloride is reduced to 0·8–2 p.c. It is then refined by dissolving it in washings of the pure salt to sp.gr. 1·53–1·55, filtering as above, and running it into iron coolers; in doing this, a very small quantity of ultramarine is added, to neutralise the discoloration produced by iron. Here a mother-liquor of the following composition is produced:

	a	*b*
Potassium nitrate . .	20·91	23·4
Sodium nitrate . .	1·02	—
Sodium chloride . .	5·94	4·4
Sodium sulphate .	0·12	—
Magnesium chloride . .	0·78	1·1

(*a*, sp.gr. 1·184 at 17°; *b*, sp.gr. 1·180 at 18·5°).

The crystals produced at the same time still contain 0·25 to 0·75 p.c. NaCl, and must be purified by washing them with water in copper-lined iron vessels, in the manner described

above for potassium chloride; this produces a liquor of sp.gr. 1·075–1·083. The washed salt is drained, and is dried upon shallow, circular cast-iron pans, heated by means of internal steam channels; a revolving shaft moves the salt about by means of scrapers forced down by springs, and a conical roller at the same time crushes any lumps formed in drying. Each pan dries nearly 4 tons of nitrate in 24 hours. Unavoidably, some crusts are formed at the bottom, which must be knocked off once a day. The dried saltpetre need only be passed through a sieve to be ready for packing into casks.

It is asserted that, when German muriate of potash is employed, traces of magnesium chloride may remain in the saltpetre and render it deliquescent; this is to be counteracted by adding as much soda-ash as will throw down the magnesia. Muriate of potash made from kelp contains no magnesium chloride, but from 6 to 8 p.c. of sulphate, which does not decompose with nitrate as easily as the chloride. In Germany the above-mentioned drawback has never been found; nor can it be conceived that a mode of manufacture which actually brings down the total chloride to 0·01 p.c. should leave anything whatever of the extremely soluble magnesium chloride in the saltpetre.

The 'saltpetre salt'—that is, the impure sodium chloride formed in this manufacture—contains about 98 p.c. of NaCl in the dry state, with 0·25 to 0·9 KNO_3 and slight quantities of other matters. The nitrate makes it unfit for decomposing with sulphuric acid on account of the strong action on the iron pans; it is used for agricultural purposes, and for roasting the cinders from cupreous pyrites in the process of copper-extracting by the wet method.

Potassium arsenate KH_2AsO_4 (Macquer's salt) is manufactured by fusing together equal parts of potassium nitrate and white arsenic (arsenious oxide), dissolving the mass in water, and evaporating; on cooling the liquor the arsenate crystallises out in large, soluble, quadratic crystals, which do not deliquesce in the air. This salt is used in calico-printing as a substitute for cow-dung.

Potassium dichromate *v.* art. CHROMIUM.

Potassium cyanides, ferrocyanide and ferricyanide, *cf.* CYANIDES.

Potassium phosphate. The Stassfurter Chemische Fabrik vorm. Vorster and Grüneberg (D. R. P. 84954) decompose calcium phosphate with sodium sulphate, remove the precipitated gypsum, add to the solution of sodium phosphate the theoretically required quantity of potassium sulphate and cool down to +4°; Glauber's salt crystallises out and the solution contains potassium dihydrogen phosphate KH_2PO_4. G. L.

POTATO, *Solanum tuberosum* (Linn.). This plant, a native of America, is grown for the sake of its underground tubers or thickened stems. These contain large stores of starch and other formative materials intended as nourishment for future plants. Each tuber has several 'eyes' which are compound buds, capable of producing one or more stalks. Many varieties are known, differing in colour, size, shape, and composition.

The following figures illustrate the variation in composition which has been observed:—

Water	Protein	Fat	Soluble carbo-hydrates	Crude fibre	Ash
68–82	0·5–3·5	0·05–0·80	12–26·5	0·3–1·4	0·4–1·5

The average composition (König) may be taken as—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
75·8	1·8	0·2	20·5	0·7	1·0

Of the total nitrogen, about half exists in non-proteid form, chiefly as asparagine, solanine, leucine, xanthine, and tyrosine. The proteids of the potato consist of a globulin—*tuberin*, soluble in dilute salt solution and showing coagulation on heating, incipient at about 60°, but not complete until 80°, and a proteose (Osborne and Campbell, J. Amer. Chem. Soc. 1896, 18, 575). The characteristic poisonous constituent of potatoes is *salanine* $C_{52}H_{93}NO_{18}$, a crystalline substance melting at 244° and almost insoluble in ether and alcohol. It is decomposed by dilute HCl, yielding *solanidine* $C_{40}H_{61}NO_2$ (m.p. 191°), soluble in hot alcohol, and a sugar (Firbas, Monatsh. 1889, 10, 541). An amorphous substance—*solanëine* $C_{52}H_{83}NO_{13}$—which also yields solanidine when heated with hydrochloric acid, and which is apparently the anhydride of solanine—is also present in the shoots of the potato.

The sugars formed by the hydrolysis of solanine are dextrose and rhamnose, according to Zeisel and Wittmann (Ber. 1903, 36, 3554), whilst Votoček and Vondraček (*ibid.* 1903, 36, 4372) showed that galactose is also produced. This was confirmed by Wittmann (Monatsh. 1905, 26, 445), who also observed the formation of a dextro-rotatory sugar which he thought was probably a polysaccharide.

According to Heiduschka and Sieger (Arch. Pharm. 1917, 255, 18) solanine has the composition $C_{52}H_{91}O_{18}N$, and forms a crystalline hydrochloride, m.p. 212°, while solanidine melts at 207°, and has the composition

$$C_{34}H_{57}O_2N$$

They think that one molecule of solanine, on hydrolysis, yields one molecule each of solanidine, dextrose, galactose, and rhamnose.

According to Wintgen (Zeitsch. Nahr. Genussm. 1906, 12, 113), the amount of solanine in potatoes is very small, the highest and lowest amounts found being 0·1059 and 0·0172 parts per thousand. No increase in the amount was observed after prolonged storage, even in germinated potatoes when the shoots were removed. He concludes that the amount of solanine is so small that no poisonous effect need be feared.

Nevertheless care should be taken that animals do not eat the young shoots of sprouted potatoes, for they have been found to contain as much as 50 parts of solanine per thousand. Potatoes, greened by the action of light, also may contain as much as 3 times the normal proportion of solanine (Kellner). According to Weil (Arch. Hygiene, 1900, 38, 330), certain bacteria induce the formation of solanine in potatoes. Some samples of potatoes contained 0·38 p.c. of solanine.

Of the nitrogen-free extract, starch constitutes the greatest portion, but sugar (varying

from about 0·5 to 1·2 p.c.) and pentosans are also present. The starch occurs in large grains —the largest from 75μ to 110μ in length—of an oval, ovate, ellipsoidal or conchoidal outline, possessing a distinct hilum, generally situated in the narrow end of the grain and with well-marked, concentric striations. Potatoes also contain small quantities of free acids, among which citric, succinic, and oxalic acids are probably the chief.

For many purposes, the commercial value of potatoes depends upon their content of starch, and it is found that this may be deduced with sufficient accuracy (to about 1 p.c.) from a determination of the specific gravity of the tubers. This can be done by means of specially designed balances, capable of weighing about 5 kilos. of potatoes in air and in water. According to tables calculated by Behrend, Marcker, and Morgen, the correlation between specific gravity of the tubers, proportion of total dry substance, and starch content, is as follows :—

Specific gravity	Percentage of dry matter	Percentage of starch
1·080	19·7	13·9
1·085	20·7	14·9
1·090	21·8	16·0
1·095	22·9	17·1
1·100	24·0	18·2
1·105	25·0	19·2
1·110	26·1	20·3
1·115	27·2	21·4
1·120	28·3	22·5
1·125	29·3	23·5
1·130	30·4	24·6
1·135	31·5	25·7
1·140	32·5	26·7
1·145	33·6	27·8
1·150	34·7	28·9

Obviously such a table can only claim approximate accuracy since the proportion of starch to other solid matter is variable in different tubers.

Balland (Compt. rend. 1897, 125, 429) found, as the result of the examination of a large number of varieties of potatoes grown in France, the following :—

	Weight of tuber grms.	Water	N-compounds	Fat	Starch and sugar	Fibre	Ash
Maximum	420·0	80·0	2·8	0·14	29·9	0·7	1·2
Minimum	23·0	66·1	1·4	0·04	15·6	0·4	0·4

The ash generally contains traces of manganese. The acidity varied from 0·07 to 0·25 p.c.

Forfang (Bied. Zentr. 1904, 33, 392) found as the average of ten analyses of potatoes grown in West Norway—

Water 75·6 p.c., total dry matter 24·4, starch 15·2, sugar 2·2, crude fibre 0·7, furfuroids 0·7, total N 0·4, fat 0·04, and ash 1·0 p.c.

Coudon and Bussard (Compt. rend. 1897, 125, 43) have examined the separate portions of potatoes. They find that after the removal of the skin, there are three distinct layers, differing in composition—the cortical layer containing the highest proportion of starch and the lowest proportion of water and nitrogenous matter—the external medullary layer of intermediate composition and the internal medullary layer which is richest in nitrogenous matter and water and poorest in starch. The proportion of starch in the cortical layer may be twice as great as in the innermost layer, whilst, in the latter, the amount of nitrogenous matter may be 28 p.c. higher than in the cortical layer. They state that the culinary value of potatoes is directly proportional to the quantity of nitrogenous matter and inversely proportional to the amount of starch present, and that it may be measured by the ratio between these quantities. The power of the tubers to retain their shape and size when boiled in water is determined by the proteids present and is not dependent upon the proportion or size of the starch grains or the amount of pectin substances present. The resistance to swelling up when boiled is measured by the ratio, proteid : starch, which in good varieties varies between 1 : 14 and 1 : 8·6, while in the varieties which disintegrate most it is 1 : 6 or even 1 : 4.

They conclude that for culinary purposes, the aim should be to cultivate varieties with a thin cortical layer and therefore poor in starch, whilst for industrial purposes, varieties with a thick cortical layer and a high content of starch are to be preferred.

New varieties of potatoes are continually being produced, for some of which great advantages are claimed.

In 1901, a wild plant growing in Uruguay, which was first described in 1767 by Commerson, was brought to Europe by Heckel. By cultivation, an edible tuber, equal to the ordinary potato, has been obtained, which it is claimed is immune to ordinary potato diseases, more resistant to frost, and capable of yielding enormous crops. This plant is known as *Solanum Commersonii* (Dun.) and is characterised by the large number of aerial tubers which it produces, in addition to its subterranean ones (Labergerie, Bied. Zentr. 1905, 34, 616).

The ash of potatoes, according to Wolff, contains on the average—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
60·3	2·6	2·6	4·7	1·2	17·3	6·4	2·0	3·0

Potatoes are extensively used as human food, as food for farm animals (best after boiling or steaming), and industrially, as a source of starch (*q.v.*), alcohol and fusel oil (*q.v.*).

As a food for animals, potatoes are used raw, steamed, as silage, or, recently, dried. The following figures (Kellner) show the composition of these various forms :—

—	Water	Protein	Fat	N-free extract	Fibre	Ash
Raw, medium	75·0	2·1	0·1	21·0	0·7	1·1
,, watery.	83·0	1·6	0·1	13·9	0·6	0·8
,, dry .	74·0	2·1	0·1	21·9	0·8	1·1
Steamed .	66·5	1·5	0·1	30·1	0·8	1·0
Raw, as silage	73·5	2·2	0·5	21·7	0·7	1·4
Dried . .	12·0	7·4	0·4	74·0	2·3	3·9

The haulms and 'apples' (fruit) of potatoes contain, usually, sufficient solanine to render them poisonous. They should not be used as food for animals.

Potatoes grow best in deep soils, well drained, free from acidity, and well supplied with potash and nitrogen.

For examples of the efficiency of spraying potato plants with copper compounds as a preventative of blight, *v.* Leaflet 14 of the Dept. of Agric. and Techn. Instruction for Ireland.

H. I.

POTOSI SILVER *v.* Nickel.

POTSTONE *v.* Talc.

POTTERY and **PORCELAIN.** The term 'pottery' is a very elastic one, being commonly used to indicate any article fashioned of clay (or of a mixture of clays and other mineral substances), and hardened by the application of fire. In this sense the term includes all kinds of crockeryware and such common articles as flooring and roofing tiles, drain-pipes, bricks, and crucibles; nor is there any reason why this comprehensiveness should be curtailed, for though a vase of Sèvres china and a drain-pipe are widely different when finished, they come equally well within the scope of our definition, and their production depends upon the application of exactly similar principles; the superior result obtained in the one case being mainly the result of superior elaboration and care.

Potteryware of every kind is usually divided into two great classes—

1. Simple or unglazed, such as flooring or roofing tiles, bricks, terra-cotta, primitive pottery, &c.

2. Composite or glazed, such as the ordinary forms of porcelain, earthenware, or stoneware used for domestic purposes.

This distinction is an arbitrary one, for almost every kind of pottery is capable of existing in both forms and of serving some useful purpose in each of them. The distinction is of value in so far as it helps us toward an easier conception of the term 'body' or 'paste' and 'enamel' or 'glaze'; the body being the stuff or substance of which the article is first fashioned or shaped and the glaze or enamel an external covering resulting from the formation of a vitrified coating on the body, to render it impervious to liquids or to serve æsthetically as decoration. A clear conception, therefore, of the various pottery bodies—of the processes by which they are prepared and of their relationship to each other—forms the simplest starting-point from which to review the science of the potter.

The foundation of every pottery body, without exception, is one or other of the natural clays, for the bare possibility of a pot, as we know it, results from two properties which the clays alone possess in any marked degree, viz. the property of being kneadable while moist into almost any required shape (what we call plasticity); and, secondly, the property of becoming dense, hard, and durable when fired (*see* art. Clay). While, however, the possession of these properties renders the use of some form of clay unavoidable further manufacturing qualities are required in a good body which can only be secured by the addition of other materials. Thus articles made from a natural plastic clay are apt to crack in drying, owing to the tenacity with which such clays retain the water added in working; in firing they are apt to soften a little, especially if the clay contains much iron or lime, and so lose their shape. These defects necessitate the admixture of sand, ground flint, or other aplastic or hardening materials, so as to make the body more open or less retentive of water, or to render it less liable to sink, in the firing, from partial fusion. Again, in some classes of pottery translucence is a necessary quality of the fired ware and this can only be secured by the due admixture of selected clays with suitable fusible materials, which vitrify when submitted to the heat of the pottery oven and, enveloping the minute particles of clay with which they are mixed, produce a semi-transparent material.

All the substances commonly used in the composition of pottery bodies may be divided into three classes according to their primary functions:—

1. Plastic materials: all the varieties of clay and marl.

2. Hardening or aplastic materials (Fr. *dégraissantes*): flint, sand, quartz, ground pitchers, &c.

3. Fusible materials: felspar, china stone, bone ash, lime, gypsum, barytes, artificial frits, &c.

The object of the potter is to select from the materials at his disposal such as will enable him to produce a suitable body under his conditions of working and firing; for it must be borne in mind that one and the same substance may play a different *rôle* in the body, according to the method of manufacture or temperature of firing. Thus, the addition of quartz to the body mixture of certain European porcelains produces a mass which matures at a lower temperature than the mixtures of china clay and felspar that were formerly used. Every form of pottery must be regarded as a mass of mixed silicates of indefinite composition, and the practical result depends both on the composition of the mass and the degree of chemical rearrangement that has taken place during the firing. In no cases are the chemical changes pushed to completion, or we should have a fused slag or glass, but the reactions are arrested at some arbitrary stage which practice has shown to be advisible. Chemical analysis may prove that a pottery body contains certain proportions of silica, alumina, &c., but the potter's business is to prepare such mixtures as possess sufficient plasticity and tenacity to enable articles to be fashioned and dried without undue loss, and capable, when properly fired, of yielding wares possessing the requisite durability, infusibility, colour, texture, &c.

The current classification of pottery into earthenware, stoneware, porcelain, &c., is thoroughly unscientific, for the distinctions on which it is based, such as colour, hardness and translucence, are mainly accidental and are often due quite as much to the methods of manufacture and the firing temperature as to inherent differences in the bodies themselves. It is impossible in the present state of our knowledge to draw any hard-and-fast line between the different classes of pottery; but perhaps the following classification, designed to bring out the natural relationships of the body mixtures, has as much to recommend it as any:—

First class.—Bodies containing only plastic materials, or a mixture of plastic and hardening materials. It is impossible to separate this into two classes, as the question whether any hardening material must be added depends entirely upon the nature of the particular clay. In this

class the following products would be included: bricks, flooring and roofing tiles, ordinary stonewares, and the common red and brown wares of all countries. The fired body is always opaque, moderately hard, and generally strongly coloured —red, grey, or buff.

Second class.—Bodies containing plastic, hardening, and fusible materials. The bodies of this class naturally cover a wide range according to the proportion in which the three classes of material enter into their composition. The fired products are hard, dense, generally opaque and white or pale in colour. All the better kinds of English earthenware, stoneware, granite and mortar bodies would be included.

Third class.—Bodies containing plastic and fusible materials, mainly. The most refined species of pottery—such as hard porcelain, soft porcelain (both natural and artificial), parian, jasper, &c.—belong to this class. The fired bodies are very hard, durable and translucent, and, unless stained by added colouring oxides, are white or creamy in colour.

Preparation of the body.—In the preparation of all working mixtures for the potters' use the first object to be aimed at is perfect homogeneity, and the more complex the body the more important does attention to this point become. For bodies of the first class it is usually sufficient to remove stones and other hard foreign matters and then pass the material through a pug-mill or mortar-mill to secure sufficient uniformity (*see* art. CLAY); but for bodies belonging to the second and third classes, where articles of high finish and mechanical perfection of shape are required, it is necessary that all the materials be reduced to a very fine state of sub-division in order to bring about their intimate admixture. The processes for this purpose are much the same for all classes of body mixtures, and it will only be necessary to describe the methods used in the preparation of English earthenware (in many respects the most complex of all) as they are quite suitable, with slight modifications in detail, for the preparation of all other bodies.

The substances used for this particular body are: ball clay from Devon or Dorset, china clay from Devon or Cornwall, china stone from Cornwall, and boulder flints from the sea beaches of Dieppe, Treport, &c. The clays used vary greatly in plasticity, and the proportion of stone or flint with which they are mixed depends largely upon this quality of the clay. The proportions used for the average cream-colour body are: ball clay, 50 p.c.; china clay, 10 p.c.; flint, 37 p.c.; china stone, 3 p.c. The clays are beaten up to a pulp with water in a blunger or iron chest in which a shaft carrying broad-bladed knives is rapidly rotated. This fluid paste is known technically as 'slip.'

The flint and stone must be reduced to impalpable powders, in order that their particles may be uniformly diffused among the particles of clay in the slip. The flints are first calcined, usually in specially constructed kilns; this calcination having rendered them white and friable, the nodules are then broken into coarse lumps in an ordinary stone-crushing machine and finally charged on to a pan similar to the one shown in section in Fig. 1.

The pan is built up from the floor, either with iron sides or with wooden staves strongly hooped together. The bed or bottom (*d*, Fig. 1) is a pavement of chert stones from 8 to 16 ins. thick, according to the size of the pan. Over the face of this pavement large blocks of chert, weighing a ton and over in the case of large pans, are driven round and round by the arms (*c*) fixed on a vertical shaft (*a*). The fragments of calcined flint, or other material to be ground, are charged on to this pavement (*d*), a little water is run in and a grinding of longer or shorter duration, according to the weight of the grinding stones, suffices to reduce the material to fine powder in suspension in water. This form of pan is extensively used for the grinding of all classes of pottery materials, such as flint, stone, felspar, glaze, &c., that are required in a state of powder. The stones of the pavement and the runners are, of course, worn away; hence it is advisable to have them of some substance whose introduction into the body in small quantities will not cause any serious disturbance of its properties. Chert paving stones and runners are obtained in the districts round Mold and Chirk in North Wales, from

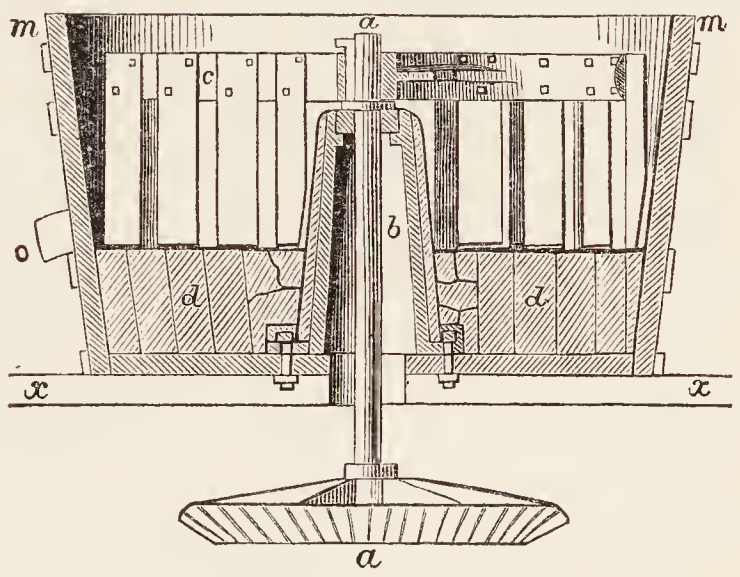


FIG. 1.—GRINDING PAN.

x. Floor line. *m*. Pan sides. *d*. Pavement of chert. *a*. Driving shaft, working in centre tub *b*, and carrying arms *c* which drive large blocks of chert over the face of the pavement *d*.

the Bakewell and Bradwell districts of North Derbyshire, and blocks of massive quartzite are also quarried in the neighbourhood of Oban, in Achill Island and in the vicinity of Cherbourg. In the pans for grinding china-stone, blocks of hard china-stone are often used both as pavers and runners. A pan of this description, 12 ft. in diameter, and carrying a load of from 5 to 6 tons of runners, should grind 1 ton of calcined flints in 12 hours. In recent years grinding cylinders of various types have to some extent replaced this type of grinding pan. An iron cylinder, lined with blocks of quartzite, stoneware, or porcelain, and provided with a manhole for the introduction and removal of the charge, is mounted on bearings so that it can be rotated. The material to be ground (flint, felspar, fritt, &c.) is charged into the cylinder in a coarse powder, such as is obtained by passing it through a crusher or edge-runner pan and a charge of flint pebbles or other suitable pulverising material is added. The manhole is then tightly closed and the cylinder rotated, when the moving charge of pebbles and material gradually reduces the latter to

an impalpable powder. The material can either be ground dry or, perferably in most cases, with water. (For discussion of 'dry' and 'wet' grinding and of 'pan' and 'cylinder' grinding, *see* the various papers in The Transactions of the English Ceramic Society, and especially Studies on Cylinder Grinding, Mellor, Trans. Eng. Cer. Soc., 9, 50 *et seq.*).

To avoid waste of time and power in the 'wet' grinding of such materials, a process of elutriation is used. It is obvious that when a charge of material is ground the efficient work must be completed in a certain time and further grinding is, largely, wasted. At this stage the material is run off the grinding pan or cylinder in varying grades of fineness, mixed with two or three times its bulk of water and thoroughly agitated. The mixture is allowed to settle, and, by the simple process of drawing off successive fractions from a settling tank (known as a wash-tub), the finer particles are drawn away for use and the coarse particles are collected as residue and returned for re-grinding. The question of the size of particles of such materials as flint, quartz. &c., is of great technical importance (*see* papers in The Transactions of the English Ceramic Society and The American Ceramic Society).

Having thus obtained all the materials in a fine state of sub-division and in suspension in water, each is run into a separate vat, the cubic contents of which are known. The specific gravity of each of the 'slop' liquids is ascertained and the proper quantities are mixed in a big vat or blending ark and thoroughly agitated. Such a mixture is known as 'slip.' This method of slop blending—at best a rough volumetric one—though in general use, needs very careful supervision in order to obtain accurate results. Alternatively, the ground and dried materials are each separately weighed and then agitated together in water. The difficulty of this method, which at first sight looks simple, is to obtain the materials in a state of consistent dryness, for clays which are apparently dry retain 2 or 3 p.c. of water. In very precise work the latter method is preferable; on the manufacturing scale the former is sufficiently accurate.

When the materials have been made into slip they are carefully sifted through fine sieves of brass, silk, or phosphor-bronze to remove all coarse particles, dirt, &c., and then finally 'magneted' to remove any particles of metallic iron, or of magnetisable iron compounds, which may have come in by way of the materials or from the machinery, and which, if left in the paste, produce black specks, a quite unsightly disfigurement in white bodies. In this country the 'magneting' is done by running the slip through a box or spout containing a number of horse-shoe magnets suspended so that they nearly touch the bottom; or electro-magnets are used. Twenty years ago such methods were in their infancy, but during that time many ingenious devices for sieving and electro-magneting have been invented for dealing with potters' materials at various stages of their preparation. The slip mixture, thus cleansed, is in condition to be made into potters' clay. Two methods of doing this are in widespread use. The older method is one of evaporation, in which the slip is run into shallow brickwork tanks (slip-kilns) to a depth of from 6 to 8 ins., and then dried to the proper consistency by fires burnt under the tanks or by coils of steam-pipes. This process is now only used where small quantities are to be operated on, where many different bodies are made, or where the nature of the mixture is such as to render the removal of small amounts of soluble salts undesirable. Clay made in this way must be carefully beaten together to render it of uniform consistency, for it is liable to contain hard lumps that have been burnt from contact with the brickwork; the process, too, is slow, and therefore quite inadequate for the production of the large quantities of clay required in the great pottery works of England and other countries. The method now adopted in all works where large quantities of clay are required is one of filtration under pressure. The slip is delivered, by force-pumps working at pressures up to about 76 lbs. on the square inch, into strong canvas bags supported between fluted wooden or iron trays securely clamped together. The bags expand a little until they fill the space between each pair of trays and then act as filters, the water being driven through the pores of the cloth and a mass of plastic clay left behind. The time taken up in this process depends upon the nature of the body; bodies like those of porcelain, granite-ware, &c., which contain only a small proportion of plastic material part with their added water readily; those used for many varieties of earthenware, which contain a large proportion of plastic clay, retain their water more obstinately and take a longer time to attain the right consistency. The potters' clay, as it is delivered from the filter-press, is always harder on the outside of the cake than on the inside, and it is either thoroughly beaten together or put through a pug-mill or rolling machine to render it uniform in consistency and free it from air-bubbles.

Some reference must be made to the obscure phenomena connected with what is known as the 'ageing' of prepared clays. Centuries of practical experience have shown that such mixtures improve in plasticity and working properties if they are kept for a considerable period and watered, beaten, and turned over occasionally. The probable explanation of this long-recognised fact is to be found in the modern view that clay is a colloidal substance. It has been fairly well established that the plasticity of a clay or clay mixture is determined by the amount and nature of its colloids. The action of relatively small amounts of acid or alkaline substances on clay is thus explicable; likewise the fact that the addition of certain colloids—such as glue, size, or soap in ancient practice and tannic acid or tannates in modern work—has proved of value in improving the working properties of a clay mass. Another practical outcome of the action of dilute alkalis on clays will be referred to in connection with the latest methods of casting pottery (*q.v.*).

The body being ready, then, for the hands of the potter, some consideration must be bestowed on the methods of shaping the desired articles from it, for these methods vary both with the shape and the size of the article and with the nature of the body. For round articles and with plastic mixtures a very old process—that of 'throwing on the wheel'—is generally

adopted; but for articles of oval or irregular shape, or with bodies of slight plasticity, other methods must be used and of these the most important are pressing and casting.

Pressing is a technical term applied to two distinct processes: (*a*) plastic pressing, in which the article is made from moist clay; (*b*) dry pressing, in which the article is stamped out of clay dust. In plastic pressing the clay is beaten or rolled out into a thin cake or 'bat,' which is then pressed by the workman into moulds of plaster of Paris or baked clay (exceptionally of sulphur or metal), which are generally made in sections so as to be readily taken to pieces. When each section of the mould has had a bat of clay applied to it and rubbed down into all its lines and indentations, the portions are fitted together, tightly strapped up, and the seams or joints are smoothed down so that the clay forms one piece inside the mould. On standing, the clay dries a little so that it contracts slightly and thus releases itself from the mould; when it is sufficiently hard to bear handling the mould is taken apart and the piece removed; its seams and edges are trimmed down and sponged smooth and it is put to dry in a hot-air stove, preparatory to firing. Many articles of pottery are now made, commercially, by pressing plastic clay mixtures in a die or through a 'template' of the required shape by mechanical power. This process is known as 'compression.' It is largely used for the manufacture of drain or sewer-pipes, or, with suitable modifications, for bricks, roofing tiles, building blocks, crucibles and similar articles. The enormous quantities of tiles used in the internal decoration of buildings are prepared by the 'dry' pressing process. The body, after a careful preparation as detailed above, is taken from the filter press, dried, and then ground to powder in a disintegrator or between rollers or mill-stones. This powder or clay-dust is slightly damped so that if a handful of it is squeezed it adheres loosely together. It is filled into a metal mould, a die is forced down upon it by hand- or mechanical-power and the tile is thus stamped from the clay dust. Such a tile possesses sufficient adhesion to bear the handling necessary to fire it and when fired it becomes hard and sonorous, though not quite so hard or durable as a tile made from clay by the old plastic process.

Casting.—The third method in general use for the fabrication of pottery articles is the simplest of all methods and is mostly used for those mixtures which do not yield a very plastic body, such as those required for the ordinary porcelains and parians. The mixed slip is not made into clay, but, after being got to such density that a pint of the fluid mixture weighs about 30 oz., it is poured into moulds made of plaster of Paris. The plaster, being porous, absorbs the water from the 'slip,' and a thin coating of clay is deposited on the inside of the plaster mould. When this coating is of sufficient thickness the remaining slip is poured out and the mould and its clay cast are set aside to drain. After the superfluous slip has drained away the mould is placed in a hot-air stove; the cast shrinks away from the mould and can then be drawn out (or the sections of the mould are removed from it), smoothed off, thoroughly dried, and the cast article is ready for the firing process. For an account of the application of compressed air, &c., to enable large pieces of porcelain to be cast, *see* Auscher, 'Technologie de la Céramique,' pp. 158–159.

A striking instance of the application of scientific method to ancient practice is shown in the most recent developments of the casting process. The method of casting pottery seems to have been invented by the Staffordshire potters of the period 1740–1750, and they soon learnt that the addition of a dilute alkaline solution such as that of sodium carbonate, enabled them to 'cast' mixtures that were otherwise impracticable. In 1891, Goetz was granted a German patent for this application (D. R. P. 76247, 1891), and this was hailed as a remarkable discovery though it had long been known in England and France. The method has, however, become of great practical importance, for the addition of dilute solutions of alkaline substances (soda, potash, waterglass, &c.) to an ordinary clay mixture enables the potter to use a clay slip at 36 oz. to the pint, containing, therefore, only about 30 p.c. of water instead of about 50 p.c. of water contained in slip at 30 oz. to the pint. This slip pours better and is freer from bubbles of air than ordinary slip and the method is now extensively used in the manufacture of large sanitary pieces, glass-pots, building blocks, saggers, &c., for it can be used either with ordinary clay mixtures or with those to which coarse materials, such as 'grog,' ground pitcher, &c., have been added. Its use also allows the fabrication of tea-pots, jugs and other intricate shapes in one piece where, formerly, the articles had to be made in three or four separate moulds. This action of dilute alkaline solutions is explained by supposing that the clay colloids have been changed from 'gel' to 'sol' (*see* J. W. Mellor, &c., Trans. Eng. Cer. Soc. 1906–1907, p. 161 *et seq.*).

Though applied with slight difference of detail to suit different bodies, and with the introduction of much machinery for the saving of labour, these three methods of throwing, pressing and casting comprise in principle all the methods used in the shaping of pottery. (For details of the processes in actual use, *v.* works mentioned in the bibliography.)

The following table exhibits in percentages the composition of the most important bodies in general use:—

Sèvres Porcelain (hard procelain): kaolin 48, felspathetic sand 48, chalk 4.

Berlin Porcelain (hard porcelain): kaolin 75, felspar 25.

Meissen Porcelain (hard porcelain): kaolin 73, felspar 25, ground porcelain pitchers 2.

Vienna Porcelain (hard porcelain): kaolin 72, felspar 12, quartz 12, gypsum 4.

English Bone China: china clay 25, china stone 25, bone ash 50.

English Cream-coloured Earthenware: ball clay 50, china clay 10, flint 35, stone 5.

English White Earthenware: ball clay 25, china clay 32, flint 34, stone 8, oxide of cobalt 0·05.

English White Tile Body: ball clay 28, china clay 28, flint 40, stone 4.

English Granite Ware: ball clay 25, china clay 25, flint 40, stone 10, oxide of cobalt 0·08.

English Terra-cotta: red marl 90, flint 5, Cornish stone 5.
English Parian: china clay 36, felspar 64.
English Mortar Body: ball clay 25, china clay 20, stone 55.
English Evaporating Pan Clay: ball clay 25, china clay 14, stone 46, flint 15.
English Fine White Stoneware: ball clay 25, china clay 20, flint 10, stone 45, oxide of cobalt 0·02.
English Black Clay: red marl 75, oxide of manganese (MnO_2) 6, calcined clay ironstone 19.
French Silicious Faience: china clay 24, chalk 24, flint or sand 48, fritt 4.
Fritt for above: sand 85, potassium carbonate 7, sodium bicarbonate 3, whiting 5.
French Tile Body: ball clay 25, chalk 25, sand 15, crushed firebrick 35.

These mixtures are extensively used, but, as already said, the potter of every country must use in practice such clays and other substances as are readily procurable to meet his particular requirements. The history of pottery shows how much the potters of every time and country have been influenced in their doings by the materials at their command. How profoundly the final result is influenced by methods of treatment may be seen from the following table, where the chemical composition of the most important modern species of pottery is shown:—

——	Silica	Alumina	Oxide of Iron	Lime and Magnesia	Alkalis
	P.c.	P.c.	P.c.	P.c.	P.c.
Ordinary stonewares . . .	68–75	20–25	2–10	1–2	2–5
Fine white stonewares . . .	70–75	20–25	0·2–1	0·5–2·5	3–5
English earthenwares . . .	66–75	17–28	0·1–1·5	0·5–2	2–3
Hard porcelains .	60–75	19–33	0·1–1	0·5–1	2·5–5

The old view of the classification of pottery bodies seemed to imply that, given a certain percentage of silica, alumina, &c., we had a complete explanation of the differences between earthenware, stoneware, and porcelain. The above table, which represents the reduction of hundreds of analyses, together with a great mass of other facts, serves to show that the chemical composition is of minor importance compared with (*a*) the chemical and physical constitution of the materials used; (*b*) the amount of re-arrangement that the conditions of firing and its final temperature ultimately produce.[1]

Firing of the body.—The firing of the ware is one of the most important branches of the potter's business, for the durability and economic value of any kind of pottery largely depend upon this factor. Each mixture requires a different method of firing, or a different degree of heat, to yield the best result. As a general rule, bodies of the first class do not require so much heat as those of the second class, nor those of the second so high a temperature as those of the third class. A clear red heat (800°–900°) is quite sufficient, for instance, for the burning of ordinary bricks; the bodies of the second class require a white heat (1150°–1250°); whilst of the bodies included in the third class, English bone china, requires about 1250°, and hard porcelain requires still higher temperatures (1300°–1500°), varying according to the composition.

Bricks, common tiles, drain-pipes and other coarse pottery are exposed directly to the flames and may, indeed, be burnt in heaps or clamps, though burning in kilns or ovens is now largely superseding the old wasteful method of burning in the open. For the finer bodies, however, such as those of the second and third classes given above, direct contact with the flames, except when the articles are to receive a salt-glaze, is generally inadmissible and such articles are therefore inclosed, or carefully packed, in fireclay boxes known as saggers (Fr. *cazettes*), which are piled one upon another—each pile of saggers being called a 'bung'—in a large chamber built of firebrick. Such a chamber forms a kind of vertical reverberatory furnace and the flames play directly into it. The particular form of furnace used, the methods of firing, and the sequence of operations are so different in the case of hard porcelain from those employed with other species of pottery that they demand a separate notice.

Hard porcelain is one of the most distinct types of pottery, but owing to the lack of sufficiently refractory fireclay and to various other causes, many of them economic, its manufacture has never obtained a permanent foothold in this country. In various European countries, as well as in China and Japan, it is extensively manufactured and in the table given above will be found the composition of the bodies used at the imperial factories of various countries. From the composition of these mixtures it is obvious that they can possess only a relatively low degree of plasticity and the manufacture of large and elaborate pieces becomes difficult and costly. Technically, the most distinctive feature of this form of pottery, whether we are dealing with the products of Europe or the Far East, lies in the fact that the body and glaze are fired together at a high temperature. In other important species of pottery, except salt-glazed or once-fired wares where the temperature is not so high, the body is first fired to a high temperature, which produces durable 'biscuit' pottery, and then, at a subsequent operation, a coating of fusible materials is melted over the surface. The fine, white earthenwares of English manufacture have, practically, the same ultimate chemical composition as porcelain (*v.* table above), but the firing temperature is not sufficient to bring about the molecular re-arrangement that we may call 'porcelainisation,' though it is quite sufficient to produce a distinct species of pottery possessing some useful qualities that porcelain lacks. In hard porcelain the manufacturer must use mixtures and processes by means of which the body will 'porcelainise' and the glaze mature at one and the same temperature (*v.* Burton, W., Porcelain, &c., 1906, chap. i. *et seq.*). A pottery mixture becomes 'porcelainised,' probably when the chemical and molecular re-arrangements have proceeded so

[1] It must not be assumed that all pottery bodies have compositions which lie between these figures; these are only typical of large and important groups.

far towards fusion that, instead of an indefinite mixture of aluminates and silicates with free silica, a stage is reached in which definite silicates are formed and the preponderance of certain crystalline or micro-crystalline compounds confers on the fired mass optical and other physical properties which have, for centuries, been recognised as distinguishing the porcelains (very indefinitely) from other kinds of pottery.

When the articles have been shaped, they are air-dried (Chinese practice), or are fired to a comparatively low heat, *feu dégourdi* 700°–900° (Japanese and European practice), in a globe or chamber (B, Fig. 2) placed over the oven proper and heated by the waste heat from it. By this latter operation the articles are completely dehydrated and rendered hard enough to take a coat of glaze with less risk of breaking. The glaze consists generally of felspathic minerals similar to those used in compounding the body

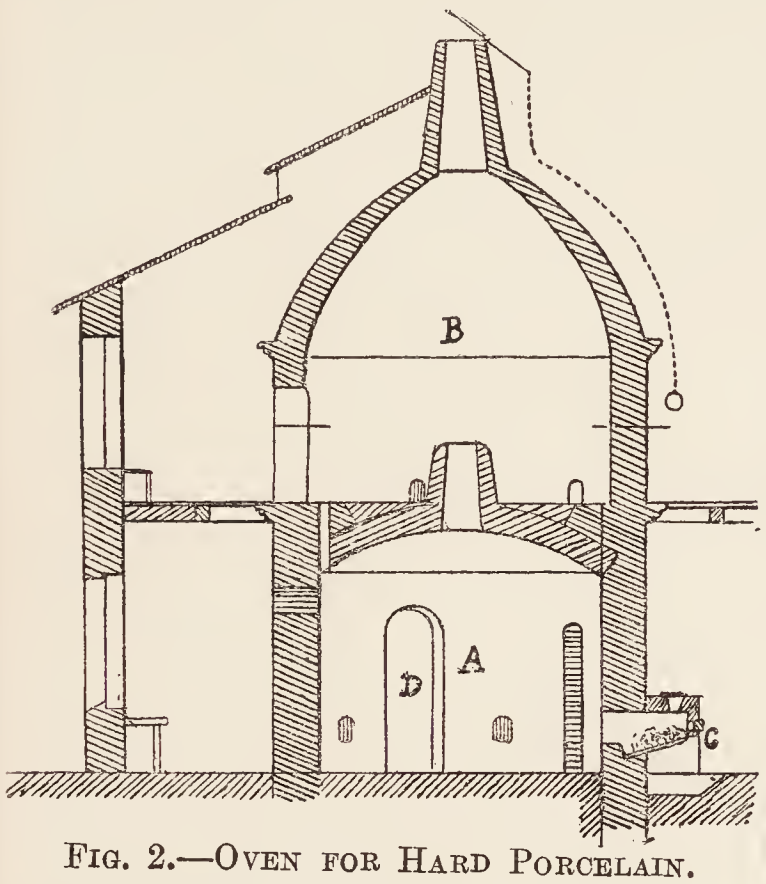


FIG. 2.—OVEN FOR HARD PORCELAIN.

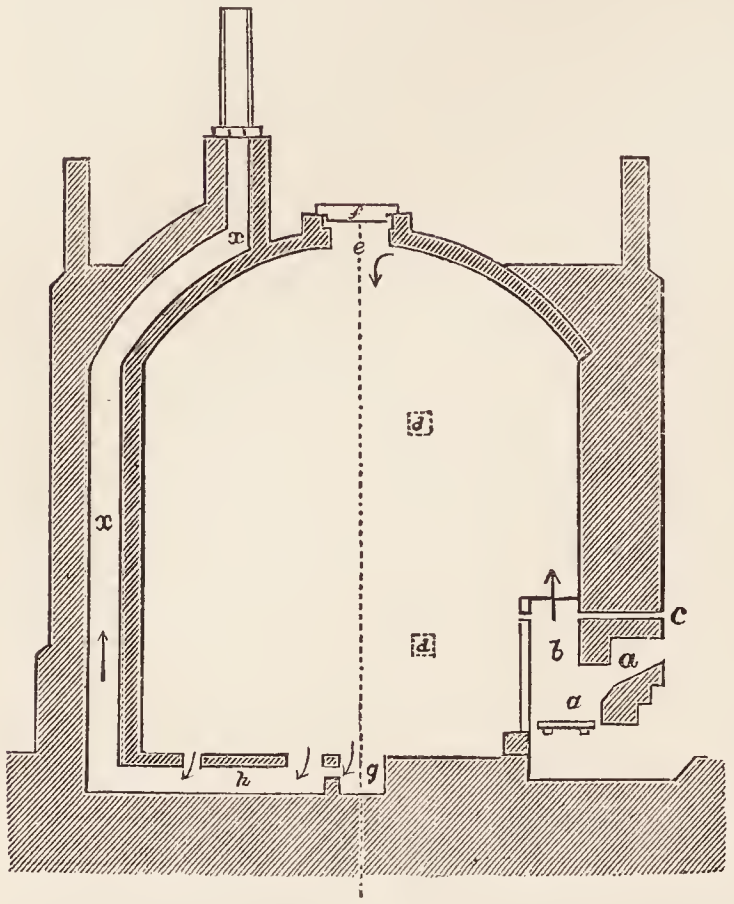
A. Oven proper. B. Globe where the ware is hardened before glazing. C. Mouth or fireplace. D. Door.

or of mixtures of felspar, quartz, &c. (*v. Glazes, infra*), ground to fine powder and held in suspension in water. The article, whether dehydrated or air-dried, is dipped in the mixture, or the glaze is pencilled or blown on to it, and, on drying, a coating of fine glaze-powder is left on the piece. The pieces are then placed in saggers of the most refractory fire-clay, and elaborate precautions are taken to support them so that they shall not touch each other or the sides of the saggers; they are also propped and supported from certain points so as to diminish the risk of sinking out of shape in the firing owing to the partial fusion of the body which takes place. The saggers of ware are then placed in the oven (A, Fig. 2) in piles or bungs until the oven is suitably filled. The doorway D is bricked up and a fire is started in each of the mouths C, of which there are four to eight or ten at equal distances round the oven. In some cases two or more chambers are built above each other, and the gases from the first are conducted through the others in such a way that when the first oven or chamber is sufficiently fired the one above it is about half fired, so that a much smaller quantity of fuel is needed to complete the burning. The form shown in Fig. 2 is that generally used in Limoges, the great seat of the French porcelain industry. Wood was commonly used as fuel until recent times because of its long, clear flame; but nowadays coal or some gaseous fuel is used (*see* below). The firing is allowed to proceed slowly for 12 to 20 hours, so that the contained and combined water may be expelled from the body by slow and gradual stages. When the temperature reaches 600°–700° all danger of cracking or rupture of the pieces from this cause ceases, and the temperature can be raised more rapidly. Beyond this point, the silicates begin to fuse and react upon each other, and the increments of temperature must be gradual and regular until the final point is reached. Then the temperature must be maintained in a state of equilibrium for a sufficient period to allow the new compounds to mature. The firing period varies from 60 to 120 hours, after which the fire-mouths are closed and the oven and its contents are allowed to cool slowly.

Other bodies.—With all other species of pottery—except those which are so vitrifiable as to need no glaze, becoming of themselves impervious to liquids, and those which are fired and glazed at one operation without 'porcelainisation'—there are two distinct firings of the ware. In the first, known as the biscuit firing, the clay article is very strongly heated, becoming hard, compact and sonorous, and though remaining porous, it may be so durable as to serve many useful purposes. To render it impervious to liquids, or for various decorative purposes, this once-fired pottery, known as 'biscuit' or 'bisque,' receives a coating of glaze material and is refired at a sufficiently high temperature to vitrify this glaze. This second fire is known as the 'glost' fire, and is always of less intensity than the 'biscuit' fire. The ovens commonly used for biscuit-firing are shown in Figs. 3 and 4.

The form of oven shown in Fig. 3, below, and known as the down-draught oven, is an improvement on the older form (Fig. 4). Here there are no flues running from the mouths under the floor of the oven, but all the flame plays into the firing chamber by the short, upright 'bags' or chimneys (*b*). The flames go up the side of the oven to the roof or crown; but, as the damper (*f*) is closed during the firing, the flame is reverberated down through the central portions of the oven, and the smoke and waste gases are drawn out through the well-hole (*g*) and the flues (*h*), which open into the chimneys (*x*) inclosed in the wall of the oven in the space between each pair of mouths. The heat is more evenly distributed in this form of oven than in the old form (shown in Fig. 4 and described below); there is a larger yield of well-fired pottery from it, and the same quantity of pottery is fired with a smaller consumption of coal. This form of oven is, however, more costly to build, and unless the proportion of air space in mouths, chimney, and oven is carefully regulated, one portion of the firing chamber may be heated sufficiently while another part may be relatively cold. The ovens used in this

country range from 12 to 20 ft. in internal diameter, and an oven of the latter size will hold



Across one of the chimneys. Across one of the mouths.

FIG. 3.—VERTICAL SECTION OF MINTON'S PATENT OVEN.

a. Mouth. *b*. Bag or short chimney into oven. *c*. Peep-hole. *d*. Holes for drawing trials. *e*. Crown-hole, closed during firing by damper *f*. *g*. Well-hole, communicating with flues *h*, which open into chimneys *x* in the walls of oven.

about 3000 saggers, each containing from one to a score of pieces; such an oven requires about

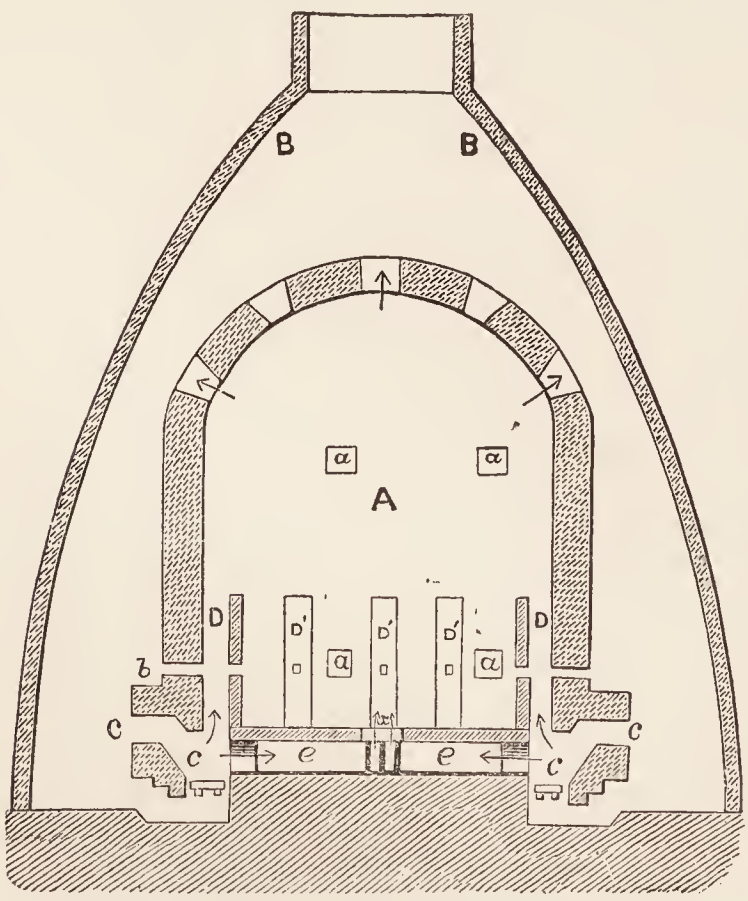


FIG. 4.—COMMON OR UP-DRAUGHT OVEN.

A. Body of oven. B. Hovel or hood. C. Mouths. D. Bag or upright chimney. D'. Other bags. *b*. Peep-hole. *e*. Bottom flues under floor of oven, running to well-hole *x*. *a*. Trial holes.

10–12 tons of coal in a firing of from 60 to 80 hours. The main points to be attended to are (*a*) firing very slowly at the commencement so as to gradually expel the water remaining in the pieces, otherwise the ware is liable to be violently ruptured; (*b*) gradually raising the heat and keeping it regular and equal in all parts of the oven and at no time either suddenly increasing or checking it.

Fig. 4 represents the old or up-draught type of oven, in which the flame from the mouths, of which there are from 8 to 10 arranged at equal distances round the oven, plays directly into the firing chamber (A) by the short, upright chimneys or 'bags' (DD). Besides these chimneys, flues (*ee*) run from each mouth to a well-hole (*x*) in the centre of the oven floor; over this well-hole a bung of perforated saggers, known as the pipe-bung, is arranged, so that a portion of the flame is drawn into the centre of the oven. The ware is bedded in sand or ground flint in the saggers, which are then piled in the oven from floor to ceiling, with spaces between the piles of saggers, or bungs, to admit the free play of the flames. Holes are left at intervals round the crown to permit the escape of the fumes and the smoke. The hovel, or hood (B), is built over the whole oven to protect it from high winds and to create a good draught. The piles of saggers being arranged in rings round the central pipe-bung, and the masses of flame playing on the walls of the oven, it follows that the centre of the oven always receives less heat then the space nearer the oven walls; it is therefore necessary to arrange the pieces in the oven in such a way that the thick or heavy pieces shall get the most fire, and the flat or thin pieces least, as they are most likely to become distorted if over-fired.

The types of oven described above, though in general use in all pottery centres, are so uneconomic that numberless patents have been granted during the last 20 or 30 years for their improvement. All the ideas underlying those patents that have not seriously modified the construction may be grouped under two headings: (*a*) improvements in the travel of the flame and products of combustion so that more energy is utilised from the fuel burnt; (*b*) the conversion of the oven-mouth into a species of gas-producer so that the coal is distilled as well as burnt. In many cases the two ideas have been combined with satisfactory results. Whatever improvements have been made in this direction, and they have already been considerable, the older type of pottery kiln must remain wasteful and unscientific from the point of view of energy consumed *versus* energy produced. The ultimate solution of the potters' problem is to be sought, probably, in the following combination: (*a*) a relatively small kiln space maintained at a constant high temperature; (*b*) methods of feeding into this chamber, at correct intervals, successive batches of pottery which have been gradually heated nearly to the temperature of the firing chamber by the waste gases passing from kiln to stack; (*c*) removal of the ware from this chamber in such a way that it is gradually cooled, imparting its heat to the advancing air-currents, which are then economically used to consume the gaseous, liquid or solid fuel for the actual firing chamber. Alternatively, where gaseous fuel is used, the firing chambers may be built in series so as to

admit of the successive introduction of (*a*) pottery, (*b*) hot waste gases for gradual heating, (*c*) air and gas for completion of firing, (*d*) air for cooling. The first method has been successfully used for years in the 'Climax' kiln for firing pottery at a comparatively low temperature as when printed, lithographed, or painted decoration has to be fired on the glazed ware; or, more perfectly, in the various types of tunnel kiln which are coming into extended use for the firing of pottery at higher temperatures. The second method has been adopted for kilns of the 'Glenboig' type (*v.* Eng. Pat. 3862 of 1881 and Eng. Pat. 17753 of 1890), and the 'Mendheim' and 'Siebert' kilns. The firing of earthenware biscuit and sanitary ware is now successfully accomplished in factories with a large output in the Shaw Continuous kiln of the Mendheim type, while biscuit tiles and similar goods are successfully fired in the Marlow Tunnel kiln. Tunnel kilns of the type of Dresslers and Marlow kilns are successfully used in the firing of majolica glazes which mature at a low temperature (about 1050°C.). (For further details, see Bourry, Traité des Industries Céramiques, 1897; Granger, La Céramique Industrielle, 1905; and Trans. Eng. Cer. Soc. vols. 2–21.)

Effects produced on pottery bodies by firing.—We must briefly consider the changes produced in a body mixture by the action of fire. The most obvious effects are changes of colour, hardness and density, entire loss of plasticity, often an increased porosity, and, practically always, a shrinkage in bulk, or contraction.

Loss of water.—The first effect of firing is the expulsion of all water left in the body. The body, before firing, contains water in two conditions: (*a*) the contained water that has been used to render the material sufficiently plastic for use; (*b*) the water of combination of its argillaceous constituents (*v.* art. Clay). The contained water is readily expelled at a temperature of about 110°, but the water of combination is not expelled in all cases by exposure to a temperature of 500°, and, with very plastic mixtures, only at a full red heat. Expulsion of the contained water causes merely a shrinkage of the body and a corresponding alteration in its density, the plasticity remains undestroyed up to that point. But when the temperature has been reached at which the water of combination is expelled, the body becomes hard and brittle, loses all its plasticity, and will no longer combine with water, however finely it may be ground.

Hardness.—One of the most notable qualities of natural clays is their property of becoming hard and durable when raised to a red heat; but in the case of pottery bodies containing other materials besides plastic ones, the degree of hardness is necessarily different from that of a natural clay heated to the same temperature. The more fusible matter the body contains, the greater is its hardness at all temperatures above that at which fusion begins, whilst bodies containing a large excess of free silica, or an excess of lime, can generally be scratched by a good knife, even after a severe fire. As a general rule, the hardness of a fired body agrees with its density, whilst it almost invariably increases with an increased temperature of firing. The following rough classification shows how the different pottery bodies stand in this respect:—

1. Scratched with a knife, readily: almost all ancient pottery and majolica (body).
2. Scratched with a knife, but with difficulty: bodies of the first class of modern manufacture.
3. Not touched with a knife, but abraded by a good file: well fired earthenware (biscuit).
4. Not scratched by a steel tool: bodies of the third class and many stoneware and mortar bodies.

Density.—The variations in density which pottery undergoes in firing are by no means well understood. With ordinary bodies there is generally an increase of density, varying with the degree of fire; but with some of the bodies of the third class the increase in density appears to be very irregular. Thus with English bone porcelain, and, according to Brongniart, in the case of hard porcelain too, although there is a considerable shrinkage of the body in firing, yet not only does the body lose weight in the firing, but it loses it at such a rate as to outstrip the loss of size so that the density of the fired body is less than that of the unfired body. English bone china, again, when overfired, suffers a great diminution in density consequent upon a sudden expansion of the article.

Shrinkage.—The contraction which all bodies undergo on firing depends upon three things: (*a*) the nature of the mixture; (*b*) the method of fabrication; (*c*) the firing conditions. Contraction due to the nature of the body either results from the expulsion of the contained water, which may cause a contraction of from 10 to 15 p.c. in those containing a very large proportion of plastic ingredients, or from the partial vitrification of the body, *e.g.* 'parian,' which contains a large proportion of felspar, contracts as much as 20 p.c. from the 'dry' to the 'fired' size. The influence of different proportions of plastic, aplastic and fusible materials in the body is well shown in the three following mixtures:—

No. 1.	
Ball clay	10 p.c.
China stone	7 ,,
Flint	80 ,,
Lime	3 ,,
No. 2.	
Ball clay	25 p.c.
China clay	10 ,,
China stone	60 ,,
Flint	5 ,,
No. 3.	
Ball clay	60 p.c.
China clay	20 ,,
China stone	10 ,,
Flint	10 ,,

These bodies were fired at 1150°, being placed in the same sagger, in the form of dry tiles pressed from dust. No. 1 exhibited no contraction, No. 2 ran in 25 p.c., and No. 3 ran in 20 p.c.

The contraction due to the loss of water connotes only physical changes, but that due to the partial vitrification of the body material generally denotes more profound re-arrangement

of the ultimate molecular structure. The effect of both these changes is strongly marked in the case of hard porcelain, which when submitted to the first or hardening fire, *feu dégourdi*, shrinks about 3 p.c. from loss of water, which is entirely expelled by this firing; but when this dehydrated ware is afterwards raised to incandescence a further contraction, amounting to nearly 7 p.c., takes place because of the interactions between the various constituents of the body.

The methods by which any given article has been shaped also modifies the amount of contraction; the ware subjected to the greatest pressure in making will contract least in firing with any given body. Moulded or pressed ware contracts less than thrown ware, and this considerably less than cast ware, although all may be made from the same mixture and fired to the same temperature.

Colour.—For the effect of fire on the colour of ordinary ferruginous clays, *v.* art. Clay, and also Appendix A, p. 267, of Catalogue of Pottery in Jermyn Street Museum. As almost all varieties of plastic clay contain sufficient traces of iron compounds to produce at least a pale cream or ivory-coloured body when fired, it is customary, in the manufacture of very white earthenware, to add a small quantity of cobalt oxide, which by the production of a blue silicate of cobalt neutralises the effect of the yellow tone due to the iron compounds; 1 part of cobalt oxide is sufficient to whiten about 2000 parts of cream-coloured body. Excess of flint or china clay and addition of lime or magnesia to the clay also whiten the fired body to a marked degree. The colour of a fired body is also influenced by the nature of the kiln atmosphere during the last stages of the firing. The whiteness of hard porcelain, although the mixture contains traces of oxide of iron, is due to the fact that the firing is finished in a reducing atmosphere. On the other hand, bricks that would burn to a deep red colour in an ordinary oxidising fire are converted into 'blue' bricks by finishing the firing in an atmosphere charged with smoke. For specially coloured bodies, *see* section on *Colours* in this article. The following table gives the percentage composition of some of the more important pottery bodies after firing:—

——	Silica	Alumina	Lime	Magnesia	Potash	Oxide of iron	Bone earth	Analyst
Sèvres hard porcelain, 1770–1830	58·00	34·50	4·50	—	3·00	—	—	Malaguti
Vienna (imperial hard porcelain), 1806	61·50	31·60	1·80	1·40	2·20	0·80	—	Laurent
Berlin hard porcelain, 1808	66·60	28·00	0·30	0·60	3·40	0·70	—	,,
Meissen hard porcelain (*dégourdi*), 1825	57·70	36·00	0·30	—	5·20	0·80	—	,,
Meissen hard porcelain (baked), 1825	59·40	32·60	—	—	5·50	0·40	—	,,
Chinese hard porcelain	70·50	20·70	0·50	0·10	6·00	0·80	—	Malaguti and Laurent
Bristol hard porcelain, 1775–1780	62·92	33·16	1·28	—	2·64	—	—	Church
English chinaware, 1847	39·88	21·48	10·06	—	2·14	—	26·44	Cowper
English chinaware, 1889	41·01	23·05	—	—	2·46	0·10	33·09	Author
English earthenware (cream colour), 1889	63·10	33·09	1·05	0·12	0·22	2·10	—	,,
English earthenware (granite), 1889	70·90	27·25	1·00	—	0·10	1·02	—	,,
English stoneware (Lambeth)	74·00	22·04	0·60	0·17	1·06	2·00	—	Salvétat
English stoneware (Wedgwood)	66·49	26·00	2·04	0·15	0·20	6·12(?)	—	,,
English red facing brick of good quality	51·01	36·90	0·24	2·01	—	9·98	—	Author
English firebrick of good quality	70·86	24·68	0·21	0·63	—	2·90	—	,,
Saggers used in Staffordshire.	68·24	26·31	0·18	—	—	4·89	—	,,

Glazes and glazing.—In discussing the various pottery bodies, it has been pointed out that some of them contain a sufficient proportion of fusible material (natural or artificial) to approach vitrification at the temperature used for manufacture. Such bodies become sufficiently impervious to fluids to serve many useful purposes, but, in the majority of cases, the body remains porous after firing and, for use or beauty, must be coated with a definite vitreous envelope or surface-layer known as the glaze.

All glazes are found to contain silica, alumina and one or more of the alkaline or alkaline-earth bases as necessary ingredients. For centuries the majority of glazes have contained lead oxide in addition, and, for the last 150 years or so, many glazes have contained boric acid as well. Chemically a glaze is a rapidly solidified solution in which silica, silicates, borates, &c., may either be solvents or solutes. For colouring or opacifying purposes metallic oxides, phosphates, &c., may be dissolved or suspended in them. If we regard a vase or a plate only, it is natural to think of the glaze as a distinct layer of glassy material melted over the surface of the pottery, but in no case is this simple view sufficient; in every case the glaze and body react with each other on fusion, and

there is always an intermediate layer of glaze-body or body-glaze, while in such instances as salt-glaze, or the common lead glazes obtained by melting lead oxide on the ware itself, the greater part of the silica and alumina needed to form the glaze are obtained from the surface of the ware by the action of soda or lead oxide at a high temperature. Between such simple types of glaze and those hard porcelain glazes which consist practically of fused felspathic rock we find every grade of chemical and physical complexity.

A perfect glaze should possess the following properties :—

1. It should be clear, brilliant, and thin, so as not to hide modelled work.

2. It should have such a suitability to and agreement with the body, as neither to chip off from the sharp edges of the body nor to break up into minute cracks (crazes) upon the surface.

3. It should be hard enough to resist wear, especially if used for culinary purposes.

4. It should not be attacked by water nor by acid vapours, and if used for culinary, domestic, or sanitary purposes should not be attacked by any ordinary dilute acid.

5. It must bear exposure to the conditions of firing and cooling, whether rapid or prolonged, without devitrification.

6. For the majority of purposes it must be so tenacious as not to run off upright objects when melted, but it must flow smoothly and evenly on flat surfaces.

7. When a glaze has to be used over printed or painted decoration, it must not have too great a solvent action on the substances used for these purposes.

8. When a glaze is to be coloured, its nature must be such that it can contain metallic compounds in solution or suspension without unsightly separations.

No glaze answers to all these requirements, but centuries of practical experience have established certain types which may be accepted as the best for their special purposes. Many ancient glazes possess certain æsthetic qualities of rare charm, but the glazes devised during the last two centuries mark a great advance in technical accomplishment. Before proceeding to the question of glazes in general, a brief account of salt-glazing is desirable.

Salt-glazing.—For the salt-glaze process only such bodies can be used as contain a considerable excess of silica uncombined with alumina. When ware of this nature is fired in a kiln with free circulation of the flame and smoke amongst it, the most expeditious method of producing the glaze is to throw on to the fires at the termination of the firing a quantity of wet salt, or it may be thrown directly into the oven. Vapours of common salt and water thus pass into the oven and a mutual decomposition takes place between them, resulting in the formation of hydrochloric acid vapours and the liberation of soda, which immediately combines with the silica and alumina of the ware, with the formation of a coating of a hard insoluble glass upon the surface exposed to the action of the fumes. It has been found in practice that clays with a wide range of composition can be successfully glazed in this way, say, where the ratio $Al_2O_3 : SiO_2$ varies from 1 : 4·6 to 1 : 12·5 ; but in general this ratio is about 1 : 8 (*v.* Trans. Amer. Ceramic Soc., 4, 211). Salt-glaze is therefore a soda-alumina-iron-silica mixture of variable composition.

Another simple type of glaze, analogous to the foregoing, is that used on the common red and brown wares of many countries, obtained by coating the unfired clay vessel with powdered galena, red lead, or litharge. In this case the molten lead oxide attacks the surface of the article and produces a rich and brilliant glaze consisting of a lead-alumina-iron-silica mixture, often containing much uncombined lead oxide.

The most important glazes are those used on the earthenwares and porcelains, for these exhibit the greatest diversity of composition and are in general use in most civilised countries. They range from the hardest porcelain glazes, consisting of little but felspar and quartz, to the softest earthenware glazes which contain silica and boric acid, together with alumina, lead oxide, lime, soda, and other bases. It is convenient to express the composition of glazes in a conventional manner so as to exhibit the ratio which the components bear to each other. This is usually done by treating the sum of the monoxide bases (reckoned molecularly) as unity and calculating the sesquioxides and dioxides proportionately. The general formula thus becomes $1RO : xR_2O_3 : yRO_2$, and it is found that x is generally less whilst y must always be greater then unity. The RO constituents may be the oxides of lead, zinc, calcium, barium, potassium, sodium, &c. ; the R_2O_3 constituent is generally alumina or alumina and sesquioxide of iron, and the principal RO_2 constituent is silica, which may in part be replaced by boric or titanic acid, &c.

It has been found that all practicable glazes lie between $1RO : 0{\cdot}1R_2O_3 : 1{\cdot}5RO_2$ and $1RO : 1{\cdot}25R_2O_3 : 12RO_2$.

It follows, from the general laws governing the fusibility of mixtures, that the more bases there are in the RO group, the lower will be the melting-point of the glaze, whilst it is equally apparent that the replacement of some of the silica by boric acid will tend in the same direction. The part played by alumina, the principal member of the R_2O_3 group, is of the utmost importance, for no stable glaze can be obtained without it, and the ratio it bears to the other constituents influences the working properties of the glaze, and especially its viscosity when melted. The hard porcelain glazes are rich in alumina and silica and comparatively poor in the members of the RO group, as we should expect from the fact that they are generally prepared from mixtures of felspar and quartz, occasionally with a little calcium carbonate. Practicable glazes of this type fall within the following limits—$1RO : 0{\cdot}2R_2O_3 : 3{\cdot}5RO_2$ and $1RO : 1{\cdot}25R_2O_3 : 12\ RO_2$, the first representing the ordinary glazes of Chinese porcelains and the last that of the most refractory European porcelains. It must also be borne in mind that in these glazes the RO group contains only soda, potash, lime, or magnesia. The glazes of earthenware and English china are widely different both in type and consitution. They include mixtures of every degree of fusibility, between 1000° and 1150° ; they have less analogy with the body than the porcelain glazes and they

are applied to 'biscuit' ware which has already been fired to a higher temperature, so that there is not the same intimate relation between glaze and body. For convenience of description, we may divide them into two groups: (*a*) raw glazes; (*b*) fritted glazes. In the first group, as all the ingredients are insoluble in water, it is sufficient to grind them together before applying the mixture to the body; in the latter, the soluble ingredients (soda, borax, &c.) must be melted with a portion of the silica, lime, or clay into a fritt or glass so as to render them insoluble in water. This fritt is then weighed out, together with the requisite proportions of flint, china stone, white lead and such other insoluble materials as are necessary, and the mixture is ground together on a pan similar to the one shown in Fig. 1, or in a grinding cylinder, until it is perfectly fine. The glaze, in suspension in water, is then put into convenient receptacles and the biscuit-ware dipped in it—a portion of the water is absorbed, and a thin coating of powdery glaze is left on the piece. The articles are placed in saggers, being carefully supported on pointed supports; the saggers are piled in bungs in ovens such as those shown in Figs. 3 or 4, and the whole is submitted to a second firing, less in intensity than the first or 'biscuit' firing, but sufficient to melt the glaze over the surface of the ware. The older form of oven shown in Fig. 4 answers better for glazing than the down-draught form shown in Fig. 3, because in the latter form the fumes and products of combustion, being kept longer in the oven, are more likely to penetrate the saggers and damage the brilliance of the glaze. It is advisable to lute the saggers together with a roll or 'wad' of clay for the 'glost' fire, so as to check the penetration of fumes into the saggers during firing. With the more fusible kinds of glaze, such as are used for the decoration of English majolica, the pieces, after dipping, instead of being enclosed in saggers, are often placed in a kiln or large muffle similar to the one shown in section in Fig. 5. This kiln takes the place of one big sagger, and the flame playing all round it raises the kiln and all its contents to a temperature sufficient for the fusion of glazes rich in lead, such as are used for these purposes. Glazes of this type approach the formula—

$$1RO : 0{\cdot}3R_2O_3 : 3{\cdot}5RO_2$$

but the RO group may contain oxides of sodium, potassium, calcium, barium, zinc, or lead, and in the RO_2 group, boric acid always replaces a portion of the silica.

Glazes that when fired may appear very similar, to any one who is not expert, may be as different as—

$$\left.\begin{matrix}0{\cdot}40\ PbO\\0{\cdot}38\ CaO\\0{\cdot}06\ K_2O\\0{\cdot}16\ Na_2O\end{matrix}\right\}0{\cdot}25\ Al_2O_3\left\{\begin{matrix}2{\cdot}75\ SiO_2\\0{\cdot}59\ B_2O_3\end{matrix}\right.$$

and

$$\left.\begin{matrix}0{\cdot}3\ K_2O\\0{\cdot}2\ Na_2O\\0{\cdot}3\ CaO\\0{\cdot}2\ BaO\end{matrix}\right\}0{\cdot}1\ Al_2O_3\left\{\begin{matrix}3{\cdot}4\ SiO_2\\0{\cdot}6\ B_2O_3\end{matrix}\right.$$

with corresponding differences of melting-point, fluidity, &c. The glazes rich in lead are more fusible and generally simpler in use than those in which the RO group comprises only alkaline and alkaline-earth bases. A leadless glaze of proved utility which matures in the glost oven has the following composition:—

$$\left.\begin{matrix}0{\cdot}3\ Na_2O\\0{\cdot}7\ K_2O\end{matrix}\right\}0{\cdot}38\ Al_2O_3\left\{\begin{matrix}3{\cdot}8\ SiO_2\\1{\cdot}0\ B_2O_3\end{matrix}\right.$$

The concentration of pottery manufacture in certain districts in each country has brought about a specialisation of the industry such as did not exist when pottery was only a handicraft. This change has caused certain evil effects of the potter's calling to need redress from statesmen and philanthropists. Lead glazes may be harmless to the worker or the user, but where occupation or use is constant, with certain glazes, some risk of plumbism follows. It is important to distinguish between the lead poisoning of the operative, caused by the use of lead compounds in glazes, and that due to lead oxide dissolved from a fired glaze by the acids used in cooking which falls on the user of the article. This latter and minor evil has not arisen in England, but in Germany an Imperial Edict has been enacted (Ref. Thorpe and Oliver, Cd. 9207 of 1899), specifying that glazes are not to be applied to articles intended for culinary use unless they will resist, when fired, the solvent action of strong, boiling acetic acid. Plumbism arising among the operatives who handle lead compounds in various manufacturing processes has given rise to many investigations in England (Thorpe and Oliver, Report to the Home Secretary on the use of Lead Compounds in Pottery, Cd. 9207 of 1899; Burton W., The Hygiene of the Pottery Trade, Shaw Lecture, Royal Society of Arts, Feb. 1908; Report of Departmental Committee, Home Office, 1908–1910, Cd. 5219, 5278, and 5385 of 1910).

The following table gives the composition of a few typical lead glazes, from the harder ones used for bone china to the softer ones used for English majolica ware:—

——	Fritt							Glaze			
	Borax	Chalk	Flint	China stone	Felspar	Soda	Kaolin	Fritt	Flint	China stone	White lead
English—											
China glaze .	50	16	40	24	33	—	—	45	—	15	15
Earthenware glaze	48	38	62	—	—	26	30	230	60	160	120
Granite glaze .	80	30	80	100	40	40	30	360	50	50	80
Majolica glaze .	40	20	40	100	—	12	—	100	—	10	120
Parian glaze .	20	—	15	20	—	—	5	20	—	—	64
Soft tile glaze .	—	—	—	—	—	—	—	—	11	22	56

These recipes might be multiplied a hundred-fold, but sufficient are here given to show the general lines of their composition, and they represent glazes in actual use.

Coloured glazes.—During the last century or so a great variety of coloured glazes have been introduced, especially for the decoration of wall tiles. The foundation of these glazes is in most cases a fritt rich in lead; and for the turquoise blues derived from cupric oxide, a fritt with a base of silicate of soda and lime. In every case the object is to get a glaze presenting a rich luscious appearance and fusible at such a low heat as not to impair by volatilization or otherwise the tone of colour produced by the addition of small quantities of oxide of copper, oxide of manganese, oxide of iron, &c. The following mixture was given by Salvétat in the Dictionnaire des Arts et Manuf., as suitable for the production of a variety of coloured glazes adapted to soft porcelain, earthenware, or tile bodies:—

Red lead . . .	2000 grms.
Flint . . .	1000 ,,
Calcium borate . .	500 ,,

This forms a colourless fusible glaze, and by the addition of the various colouring oxides any desired variety of shade can be produced. Blues by the addition of from 40 to 125 grms. of cobalt oxide to the above quantity of glaze; blue-greens by the addition of from 100 to 500 grms. of cupric oxide to the above quantity of glaze; ivory to strong yellow by the addition of from 70 to 200 grms. of ferric oxide to the above quanity of glaze; madder-brown to purple-brown by the addition of from 70 to 125 grms. of manganic oxide to the above quantity of glaze, and various intermediate tints by admixture of the different oxides in various proportions. The mixture of glaze materials and colouring oxide is ground coarsely together, melted in crucibles, poured out into water and ground fine; in this way a more perfect combination is obtained than by simply grinding the materials together. An English mixture serving the same purposes, but not quire so fusible nor so generally applicable to the various bodies as the one given above, is made by grinding together flint 100 parts, china stone 90 parts, red lead 360 parts, borax 40 parts. The mixture is fritted in flinted saggers, ground and then various proportions of finely-ground metallic oxides are added to it for colouring purposes. These glazes may be applied by dipping like ordinary glazes, but they are often applied by large camel-hair pencils or blown on by compressed air, and mingled tints produced in this way are often exceedingly beautiful.

The question of the composition and constitution of all the various types of coloured glazes is too complex to be treated here; for details the reader must refer to the more important treatises given in the bibliography at the end of the article and to the proceedings of the Ceramic Societies of this and other countries.

The stanniferous glazes, or enamels, as they are more generally called, are not so largely used now, except for the manufacture of white glazed bricks, as they were at the time of the Renaissance and later, when the famous Italian Majolica and Della Robbia wares and the Delft of Holland were decorated on a ground of opaque tin enamel. A revival of this manufacure has, however, taken place during the last sixty or seventy years; and in Italy, France, Germany, and Holland many factories still manufacture faïence with a stanniferous glaze. The following recipes are given by Deck for the principal enamels of this class:—

White.—Lead and tin ashes, 44; sand, 44; soda, 2; common salt, 8; red lead, 2.

Yellow.—White as above, 91; antimony oxide, 9.

Blue.—White as above, 95; cobalt oxide, 5.

Green.—White as above, 95; cupric oxide, 5.

Yellow-green.—White as above, 94; cupric oxide, 4; lead antimoniate, 2.

Violet.—White as above, 96; manganese dioxide, 4; although of course the exact composition of the glaze will depend upon the body to which it is to be applied.

Bodies very rich in fusible materials like parian and some of the finer stonewares, become quite impervious to liquids and acquire a smooth and glossy surface without the application of a glaze, from the semi-vitrification of the body itself. Opener and less fusible bodies than these acquire a similar surface if they are fired in saggers, the insides of which have been washed with glaze rich in oxide of lead and containing chlorides or fluorides. Mixtures of oxide of lead with cryolite, fluorspar, common salt, calcium chloride, &c., are the best for this purpose. When heated, they probably give off volatile fluorides or chlorides of lead and these are again decomposed on the surface of the ware forming a thin smear or coating of lead silicate. One of the common defects of glazes—the separation of certain compounds on cooling—has, in recent years, been cultivated so as to produce effects of rare beauty. Glazes rich in zinc oxide are apt to develop crystals of willemite (zinc silicate) on cooling. At Copenhagen, Sèvres, and Berlin, and by Doultons and B. Moore in England, the preparation of such glazes has been raised almost to a fine art. Other glazes yield beautiful small crystals of various micas and of this kind the 'Aventurine' glazes of Pilkington's, introduced by Joseph Burton, are highly esteemed (*see* Burton, W., Crystalline Glazes as Pottery Decoration, Journal Soc. of Arts. 1902).

Colours.—No department of pottery has made such advances during the last century or so as the preparation of the various ceramic colours, and while previously the colours were, for the most part, fired *on* the glaze at low temperatures, we now possess coloured bodies, under-glaze colours, and on-glaze colours in abundance. Owing to the fact that all pottery colours require to be submitted to at least a red heat, no organic colours can be used for this purpose, and recourse must therefore be had to such inorganic compounds as will produce colour effects without decomposition at high temperatures and under the solvent action of glazes and fluxes. The list of substances which answer these requirements is by no means a large one, comprising only the oxides of cobalt, nickel, iron, manganese, zinc, copper, antimony,

lead, uranium, and iridium, a few salts, such as chromates of iron, lead, and barium, the natural ochres, purple of Cassius, and a few obscure compounds such as chrome tin pink. For the preparation and properties of each of these substances reference must be made to the respective articles in this work, in which they are treated at length.

Coloured bodies. In almost every form of pottery belonging to classes 2 and 3, it is possible to stain the white bodies with various colours; but owing to the fact that they have to endure the most intense heat used by the potter, the number of colours is very limited. The bodies rich in fusible materials, especially those rich in felspar, stain most beautifully, as the felspar forms a neutral flux in which the particles of colouring matter are dissolved and so produce their richest effects. Mosaic tiles and tesseræ, coloured parians, porcelains, and jaspers are the best examples of coloured bodies. They are all rich in fusible materials. The following are a few of the proportions used:—

Blue (pale), 95 parts of body; 5 parts of cobalt oxide.

Blue (strong), 90 parts of body; 10 parts of cobalt oxide.

Green, 85 parts of body; 5 parts of cobalt oxide; 10 parts of chromium oxide.

Blue-green, 95 parts of body; $2\frac{1}{2}$ parts of chromium oxide; $1\frac{3}{4}$ parts of cobalt oxide; $1\frac{1}{4}$ parts of zinc oxide.

Bronze-green, 95 parts of body; 5 parts of calcined nickel oxide.

Brown, 85 parts of body; 15 parts of calcined iron oxide.

Yellow, 90 parts of body; 10 parts of titanium oxide.

Black, 90 parts of body; 7 parts of iron oxide; 3 parts of cobalt oxide.

In the style of decoration known as 'barbotine' or slip painting, colouring oxides are often added to the ordinary earthenware or stoneware mixtures, but the effect is much inferior in juicy richness unless the article be afterwards glazed.

Under-glaze colours. These colours, consisting for the most part of oxides, chromates, or silicates, mixed with china clay, flint, &c., so as to diminish the action of the glaze upon them, or to assist in the development of the tone of colour required, are applied on the biscuit-ware before the piece is glazed. They must therefore resist the action of the glaze at a temperature sufficient to melt the latter; they must be infusible enough to remain *still* under it; and they must have such an agreement with both the glaze and the body as not to cause the glaze to fly off in flakes. The following colours answer well for both china and earthenware:—

Black, 8 parts of native iron chromate; 3 parts of Mn_3O_4; 3 parts of CoO; 1 part of flint, calcined together strongly and then ground fine.

Dark blue, 4 parts of CoO; 1 part of flint; 1 part of chalk, ground together.

Azure blue, 60 parts of ammonium alum; 3 parts of cobalt oxide; calcined strongly, then ground and washed thoroughly until free from traces of acid.

Blue-green, 12 parts of borax; 12 parts of chalk; 12 parts of zinc oxide; 24 parts of green oxide of chromium; 4 parts of cobalt oxide; calcine well together and grind until fine.

Dark brown, 8 parts of native iron chromate; 4 parts of zinc oxide; 2 parts of iron oxide ground well together, calcined strongly and reground.

Red-brown, 6 parts of precipitated iron chromate; 20 parts of zinc oxide; 3 parts of litharge; calcine together strongly and then grind fine.

Pink colour: tin oxide, 100; chalk, 34; chromium oxide (Cr_2O_3), 1; silica, 5; mixed well together, calcined strongly, and ground.

Yellow: antimony oxide, 3; red lead, 6; flint, 2; tin oxide, 1; calcined together and then ground.

In all these colours the important point is to have the materials well ground together before calcining to promote their union, and the value of the tint is much improved if the final grinding is as complete as possible.

On-glaze colours. These colours are really fusible glasses, of such a nature that when they are applied upon the fired glaze and the article is refired at 700°–800°, they become fused to its surface. Unless this union with the glaze be perfect, such colours are always liable to wear off, and they never have the richness of under-glaze colours owing to the lower temperature at which they are fired. On-glaze colours are divided into the two classes of regular-kiln colours and hard-kiln colours, the latter colours containing a smaller proportion of flux than the former and hence requiring a higher temperature of firing.

The first requisite in on-glaze colours is a series of fluxes which shall accord well with the glaze, shall fuse at a sufficiently low temperature, and shall fuse the particles of colouring matter without decomposition. Salvétat prepared a series of fluxes which answer perfectly for hard porcelain. Their composition is as follows:—

——	No. 1 Flux	No. 2 Flux	No 3. Flux	No. 4 Flux	No. 5 Flux
Litharge .	75·0	66·66	11·12	37·50	73·00
Silica . .	25·0	22·22	33·33	12·50	9·00
Calcined borax	—	11·11	55·55	—	—
Boric acid .	—	—	—	50·00	18·00

No. 1 is a special flux for certain dark blues fired in the hard kiln; No. 2 is the general flux for browns, greys, yellows, and iron-reds; No. 3 is the flux for carmines made from gold, and No. 4 for gold-purples; No. 5 is the peculiar compound used for greens prepared from chromium oxide—a flux used for a similar purpose at Meissen was composed of 73 parts of litharge, 18 parts of silica, and 9 parts of boric acid.

The fluxes used in England differ considerably from the foregoing on account of the different types of glaze to which they are applied; in this country almost every colour-maker has fluxes of his own, and there is considerable difficulty in arriving at anything like a general statement as to the composition of

the fluxes used. The following compositions are for fluxes largely used in Staffordshire :—

——	No. 1 Flux	No. 2 Flux	No. 3 Flux	No. 4 Flux	No. 5 Flux
Red lead .	64·50	49·99	30·55	15·76	40·00
Silica . .	21·50	16·66	41·68	21·19	20·00
Borax (cryst.)	—	33·33	27·77	63·05	40·00
Flint glass .	14·00	—	—	—	—

No. 1 is a special flux for a brilliant scarlet preparation from lead dichromate; and the remainder are used for the same purposes as the similarly numbered French fluxes described before.

The preparation of all the fluxes is as follows: The various ingredients are ground together dry and then melted in good crucibles; when melted they are poured out either into water or on a slab, the latter method being preferable, as fluxes rich in borax are readily attacked by water. They are then ground to a fine powder and are ready for mixing with the colouring agent.

The following typical mixtures will serve as an indication of the general composition of on-glaze colours; the proportions of colour and flux remain good in all cases, the only point being to use a suitable flux :—

Regular-kiln colours.

Strong grey.—Flux No. 2, 68 parts; cobalt carbonate, 6; ferric hydrate, 13; zinc carbonate, 13.

Pale grey.—Flux, No. 2, 92 parts; cobalt carbonate, 5; ferric hydroxide, 3.

Strong black.—Flux No. 2, 80 parts; cobalt carbonate, 10; ferric hydroxide, 10.

Iridium black.—Flux No. 2, 75 parts; iridium sesquioxide, 25.

Uranium black.—Flux No. 2, 75 parts; black oxide of uranium, 25.

Strong blue.—Flux No. 2, 61 parts; cobalt carbonate, 13; zinc carbonate, 26.

Pale blue.—Flux No. 2, 80 parts; cobalt carbonate, 6; zinc oxide, 14.

Blue-green.—Flux No. 5, 75 parts; cobalt carbonate, 6; green oxide of chromium, 19.

Sea-green.—Flux No. 2, 80 parts; copper carbonate, 20.

Pale yellow.—Flux No. 1, 80 parts; potassium antimoniate, 14; zinc carbonate, 6.

Orange.—Flux No. 1, 80 parts; potassium antimoniate, 14; red oxide of iron, 6.

Uranium orange.—Flux No. 1, 75 parts; yellow oxide of uranium, 25.

Yellow-brown.—Flux No. 2, 75 parts; ferric oxide, 10; zinc carbonate, 15.

Red.—Flux No. 2, 75 parts; red ferric oxide, 25.

Rose colour.—Flux No. 3, 87 parts; purple of Cassius, 12; precipitated silver, 1.

Purple.—Flux No. 4, 90 parts; purple of Cassius 7; gold oxide, 3.

A scarlet-red on-glaze colour is obtained from selenium oxide and cadmium sulphide associated with a soft flux, but it is more useful for iron enamel than for pottery.

All these colours, with the exception of the last four, are made by grinding together the constituents, then fusing the mixture in crucibles, and regrinding perfectly fine. Of the remaining three colours, the red from oxide of iron needs most careful preparation. The oxide for this purpose is prepared by carefully calcining dried ferrous sulphate until the brilliant red tint is fully developed, which takes place between 400°–420°. Below this temperature a dirty yellowish-brown, and above it a purplish-brown, product is obtained. The oxide of iron and flux are simply ground together, not calcined.

The colours obtained from gold are obtained by mixing the ingredients well together, and submitting the mass to a gentle calcining at a temperature below redness; they vary in tint with the degree of heat to which they are subjected, changing from a dull rose-colour at a clear red heat to a dullish purple at a heat approaching whiteness.

Hard-kiln colours.

These colours are prepared from materials similar to those used for regular-kiln colours, but they contain a smaller proportion of flux. Owing to the greater heat to which they are subjected, the number of compounds which can be used is more limited than in the former case; but the colours become so fused into the glaze that they attain an added richness and brilliancy, and at the same time gold and other metals can be applied over them for decorative purposes.

Metals.—Only the noble metals can be applied in the metallic state for the decoration of pottery, and of these only gold, silver, and platinum are in actual use. The preparation of the gold for pottery purposes necessitates its production in as fine a state of subdivision as possible. Three methods are in use for this purpose :—

1. The French method, in which the gold is obtained in a finely divided state by precipitating a very dilute solution of the chloride with a dilute solution of ferrous sulphate (*v.* art. Gold). The precipitated gold, after careful and repeated washings, is dried and ground with $\frac{1}{12}$th of its weight of bismuth nitrate or of calcined borax; this powder is then made up into a pigment by mixing it with oil of lavender or fat turpentine, and when fired the bismuth salt or the borax serves to flux it to the glaze.

2. The English method, by which an amalgam of equal parts of gold and mercury is prepared, mixed with $\frac{1}{10}$th to $\frac{1}{12}$th of its weight of the No. 2 flux given above, and ground under water to an impalpable powder. This is dried, mixed with fat oils, and applied, like the other, and when fired the mercury volatilises, leaving the gold with a dead or matt surface, which is then brightened by scouring with sand and burnishing with agate, bloodstone, &c. Silver and platinum are seldom used by themselves but, by adding from 12 p.c. to 25 p.c. of them to pure gold, light and green golds are produced which are much prized as additional decorative resources in rich gilding.

For very elaborate and expensive work, gold is sometimes prepared by grinding gold-leaf under water with the requisite amount of flux. The powder thus obtained is dried, and ground up with honey to a workable consistency. It is applied thickly, and after firing can be chased and cut up with agate chasers. This

was the method of gilding used on the finest examples of the soft porcelain of Sèvres.

3. What is known as ' liquid ' gold is now in common use. A fluid mixture is prepared by pouring a solution of auric chloride into an oily menstrum. This may be painted, printed, or otherwise transferred to the glazed surface, and on firing a brilliant deposit of gold is left which does not need burnishing. This method is analogous to that by which the gold and silver lustres of the eighteenth and nineteenth centuries used on common pottery were obtained, the so-called ' silver ' lustre being a film of platinum (*v.* below).

Lustres.—Iridescent metallic films have been used as a means of pottery decoration since the ninth century, and the lustred wares of the Persian, Italian, and Hispano-Moresque potters (ninth to sixteenth centuries) have formed the subject of many treatises. After centuries of neglect this elegant process has been revived during the last fifty years, and, in many countries, it is again used as a distinctive pottery decoration. In principle it consists in the production of films of silver or copper on a fired glaze, but the films are of such exquiste tenuity that they glow with interference colours like a soap bubble, as well as with the yellow colour which silver, or the red colour which copper, imparts to a glaze. The term ' lustre ' has been carelessly applied to pottery covered with thin metallic films of gold or platinum (eighteenth century and later). In speaking of lustre, the term ought to be restricted to those metallic films that are so thin as to be iridescent (*v.* Burton, W., Lustre Pottery, Journ. Roy. Soc. of Arts, 1907, vol. 55). The term ' lustre ' is also commonly used for certain compounds with a bismuth salt as base, which when fired in an ordinary kiln leave pearly films, which are feebly iridescent, but these are fired at so low a temperature that they are not very durable and they always lack the artistic charm of true lustre decoration.

Application of colours.—The colours are applied by painting, stencilling, the transfer of printed or lithographed patterns, by various forms of anograph, and in a variety of minor ways. In each case the colour is mixed with a resinous medium to give it body. For printing purposes it is made into a kind of ink or pigment by mixing with thick, boiled linseed oil. The mixture is then worked into an engraving or etching on a flat copper plate or roller; the excess of colour is removed, and a print taken from the engraving on thin tissue-paper. Lithographs are prepared much in the usual way. The paper print or lithograph is then applied to the required article; in the case of under-glaze colours on the biscuit ware, and in the case of on-glaze colours on the glazed ware. The porous biscuit ware readily absorbs the colour from the paper when rubbed, and the paper can then be washed or pulled off. Glazed pieces are first ' primed ' with a size made by thinning Canada balsam with turpentine; this size serves to absorb the colour, and after standing some time the paper is washed off, leaving behind a perfect impression in colour. The ware then requires to be fired, and this firing is effected in a closed kiln or muffle, shown in section in Fig. 5. The ware is skillfully piled in this; in the case of biscuit ware it is heated to full redness to expel the printing oils, and leave the ware in a condition to receive the glaze; in the case of on-glaze colours, the firing is carefully regulated to suit the particular colours in question. During recent years much printed biscuit ware is no longer heated to drive out the oil, but the latter is practically saponified by washing the piece in a bath of dilute acid, so that a sufficient coat of glaze adheres when the pieces are dipped.

In painting, the colours, whether under-glaze or on-glaze, are mixed up into workable pigments with fat turpentine, oil of lavender, aniseed, &c., and applied with camel-hair pencils in the ordinary way.

Metals are usually fluxed, so as to adhere

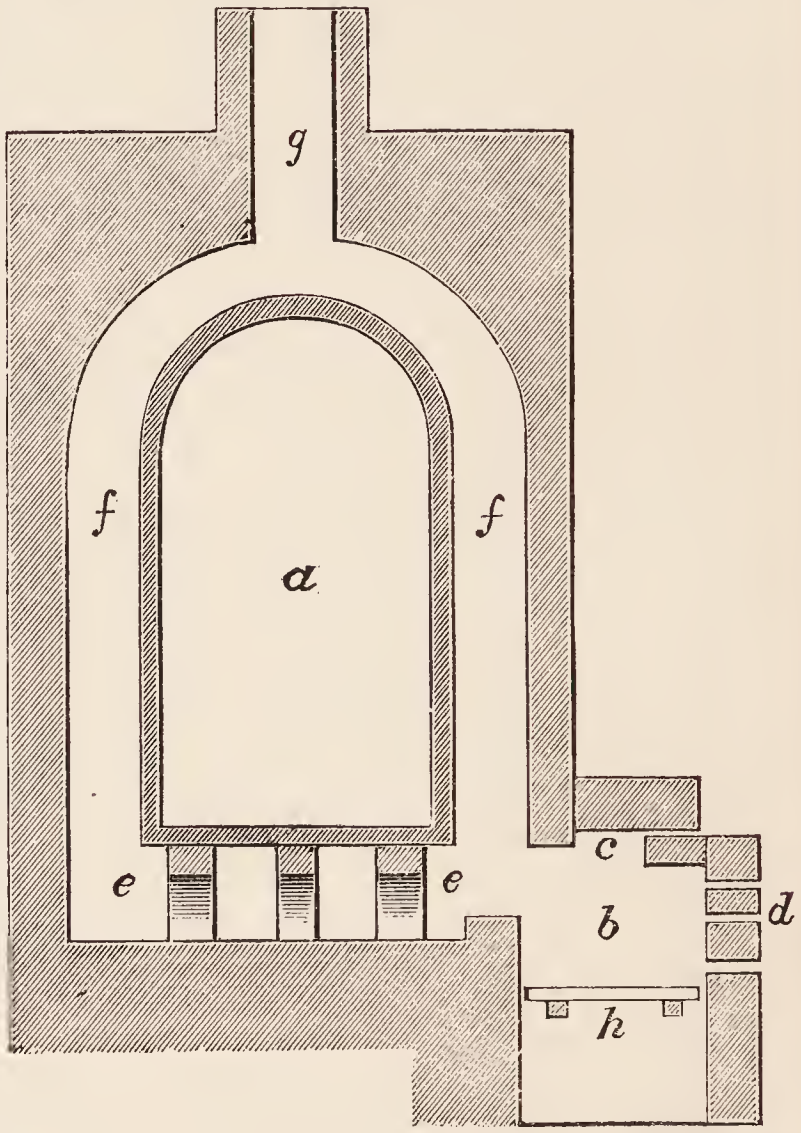


FIG. 5.—TRANSVERSE SECTION OF ENAMELLING KILN.

a. Kiln. *b.* Fireplace, charged at *c.* *e.* Bottom flue. *f.* Upright flues. *g.* Chimney.

perfectly to the glaze at the heat necessary to fire on the on-glaze colours.

Various pyrometers and pyroscopes have been devised for pottery purposes from the ' contraction ' pyrometer of Wedgwood to the fusible cones of Seger (*v.* art. PYROMETRY; also Burton, W., Trans. Eng. Ceramic Soc. vol. 6; and Darling, Industrial Pyrometry (Cantor Lectures, Roy. Soc. Arts. 1910–1911)); but in practical work the fireman usually judges the progress of the firing by small trials of a similar substance to the material being fired, which he removes from the kiln from time to time as the firing progresses.

Literature.—Brongniart's great work, Traités des Arts Céramiques, especially the edition of 1877, with additions by Salvétat, laid the

foundation of modern ideas, but is now out of date. Salvétat published many valuable essays, notably his Leçons de Céramiques. Seger's collected writings (German edition, 1895; English translation, 1902) mark an epoch because they furnished a fresh starting-point for later investigators in all countries. The Sprechsaal and Keramische Rundschau in Germany; the Comptes Rendus, and other publications of the Academy in France; Transactions of the English Ceramic Society and those of the American Ceramic Society, record current progress. A few works such as Langenbeck, Chemistry of Pottery, 1895; Auscher, Technologie de la Céramique, 1901; Bourry, Traité des Industries Céramiques, 1897, English translation, 1901; Schamberger, Die Keramische Praxis, 1901; Granger, La Céramique Industrielle, 1905; B. Kerl, Handbuch der Gesammten Thonwaarenindustrie, E. Cramer and H. Hecht's edition, 1907; and K. Dümmler, Handbuch der Ziegel Fabrikation, are convenient text-books of modern theory and practice. The Report on Pottery Industry (Dept. of Commerce, Miscellaneous Series—No 21, Washington Government Printing Office, 1915) contains some valuable data as to costs of manufacture. W. B.

POUDRE B *v.* EXPLOSIVES.

POWELLITE. Calcium molybdate $CaMoO_4$, crystallised in the tetragonal system, and isomorphous with scheelite ($CaWO_4$), wulfenite ($PbMoO_4$), &c. Bluish-green pyramidal crystals have been found in Idaho, and in the South Hecla copper mine in Michigan. These contain WO_3 1·65–10·28 p.c., replacing molybdenum, and have sp.gr. 4·35–4·52. As pearly-grey scales pseudomorphous after molybdenite (MoS_2) the mineral appears to be of much more common occurrence. Such material contains only traces of tungsten and has sp.gr. 4·25. It has been recorded from Texas, Nevada, California, and Siberia. L. J. S.

POZZUOLANA *v.* CEMENT; TUFF.

PRASE *v.* QUARTZ.

PRASEODYMIUM. Sym. Pr.; at.wt. 140·92 (Baxter and Stewart). One of the two metallic components of the rare earth 'didymia.'

Occurrence and separation v. NEODYMIUM. The metal, sp.gr. 6·4754; m.p. 940°, is obtained by the electrolysis of its fused chloride and purified by melting under anhydrous barium chloride in a magnesia crucible (Muthmann and Weiss, Annalen, 1904, 331, 1). It forms an ill-defined hydride.

Praseodymium carbide PrC_2, sp.gr. 5·10; closely resembles the neodymium compound, and is decomposed by water, yielding a mixture of acetylene, paraffins, and olefines.

Praseodymium fluoride PrF_3, yellow glistening crystals produced by mixing warm solutions of hydrogen fluoride and praseodymium nitrate (Ber. 1908, 41, 634).

Praseodymium chloride $PrCl_3$, pale green hygroscopic mass. $d25°=4·02$. Preparation, *v.* NEODYMIUM. The heptahydrate separates in large green crystals (Scheele, Zeitsch. anorg. Chem. 1898, 18, 352; Matignon, Compt. rend. 1902, 134, 427).

Praseodymium hydroxide $Pr(OH)_3$, a bright green precipitate, thrown down by caustic alkalis or ammonia from soluble praseodymium salts. In the presence of hydrogen peroxide a hydrated praseodymium peroxide, Pr_2O_5,xH_2O, is formed (Chem. Zentr. 1902, i. 172).

Praseodymium peroxide PrO_2. The higher black oxide is produced on heating praseodymium hydroxide, nitrate or oxalate in the air, but its exact composition depends on the temperature. The maximum proportion of active oxygen is taken up when praseodymium nitrate is melted with potassium nitrate at 400°–450°. The presence of cerium increases the tendency to form the peroxide, whilst lanthanum and neodymium have an inhibiting action. The peroxide liberates iodine and chlorine from the corresponding halogen hydrides in aqueous solution. In acid solutions it oxidises cerous to ceric salts, and manganous salts to permanganic acid; with hydrogen peroxide it evolves oxygen (Monatsh. 1885, 6, 477; Zeitsch. anorg. Chem. 1898, 17, 310; *ibid.* 1902, 32, 1; 1904, 41, 94; Chem Soc. Proc. 1901, 17, 66; Ber. 1892, 25, 569; 1902, 35, 2370, 3740).

Praseodymium oxide (*praseodymia*) Pr_2O_3, greenish-yellow powder, produced by heating the peroxide in hydrogen; it readily undergoes oxidation in the air, becoming brown.

Praseodymium sulphate $Pr_2(SO_4)_3,8H_2O$, monoclinic crystals, isomorphous with the corresponding hydrated sulphates of neodymium, samarium and erbium (Zeitsch. Krist. 1901, 34, 307); it is the most stable hydrate, but two others are known with 12 and 15·5 H_2O. A basic sulphate is formed by heating it to 850°.

Praseodymium nitrate $Pr(NO_3)_3,6H_2O$, deliquescent green needles; forms well-defined double nitrates, *e.g.* $Pr(NO_3)_3,2NH_4NO_3,4H_2O$ and $Pr(NO_3)_3,2RbNO_3,4H_2O$ (Zeitsch. anorg. Chem. 1911, 69, 221).

Praseodymium carbonate $Pr_2(CO_3)_3,8H_3O$, forms green double carbonates with ammonium and potassium carbonates (Zeitsch. anorg. Chem. 1904, 41, 94).

Praseodymium oxalate $Pr_2(C_2O_4)_3,10H_2O$, crystalline pale green powder; the **acetylacetonate**, $Pr[CH(CO·CH_3)_2]_3$, m.p. 146°, is bimolecular in boiling carbon disulphide.

Praseodymium dimethyl phosphate, green, hexagonal crystals, solubility 64·1 at 25°. For other salts of praseodymium, *see* Pratt and James, (J. Amer. Chem. Soc. 1911, 33, 1330); Whittemore and James (*ibid.* 1913, 35, 127); Katz and James (*ibid.* 1913, 35, 872); Morgan and James (*ibid.* 1914, 36, 10); Jantsch and Grünkraut (*ibid.* 1913, 79, 305).

Absorption spectrum of praseodymium consists of fine bands ranging from λ 597 to λ 444 (Annalen, 1890, 256, 159; Ber. 1892, 25, 569; 1900, 33, 42; Chem. Soc. Proc. 1898, 191, 71; Jones and Gray, Zeitsch. Physikal. Chem. 1912, 13, 649; Amer. Chem. J. 1913, 49, 1: *v.* NEODYMIUM).

Arc and spark spectrum, v. NEODYMIUM.

Physiological action of praseodymium salts, *v.* NEODYMIUM. G. T. M.

PRECIOUS STONES are those minerals which, by reason of their high degree of hardness, brilliant lustre, and attractive colour, combined with rarity of occurrence, find an application in jewellery. The several kinds differ widely in chemical composition; but with the notable exceptions of diamond and turquoise, the majority of them fall in the oxide (including

aluminate) and silicate divisions of the mineralogical system of classification. As indicating the range in composition, the following may be mentioned :—

Element: Diamond.

Sulphides: (Too soft; or affected by light. Pyrites is occasionally used in cheap jewellery).

Haloids: (Too soft. Fluor-spar has been used).

Oxides: Corundum (ruby and sapphire), quartz (including agate, amethyst, chalcedony, rock-crystal, jasper, &c.), opal, hæmatite.

Aluminates: Spinel, chrysoberyl.

Carbonates: (Too soft. Malachite and the satin-spar variety of calcite occasionally used.)

Sulphates: (Too soft. The satin-spar variety of gypsum and alabaster used for ornamental purposes.)

Phosphates: Turquoise, rarely lazulite and apatite.

Silicates: Andalusite, axinite, beryl (aquamarine and emerald), diopside, enstatite, epidote, euclase, felspar, garnet, iolite, jade, lapis-lazuli, olivine, phenakite, rhodonite, sphene, spodumene, topaz, tourmaline, zircon, &c.

Organic compounds: Amber, jet.

For descriptions of each of these minerals, *see* under the respective headings; *see* also GEMS, ARTIFICIAL; GEMS, IMITATION AND COUNTERFEIT. L. J. S.

PRECIPITATE, RED, WHITE, *v.* MERCURY.

PRECIPITATION, ELECTRICAL. *Historical sketch.*—In 1824, Hohlfeld of Leipzig suggested the removal of suspended particles from gas by means of electrical discharges. He found that if a wire hung in a bottle filled with smoke were electrified, the smoke cleared rapidly, and a deposit formed on the sides and bottom of the bottle. His suggestion seems to have been forgotten until about 25 years later, when C. F. Guitard of London again called this phenomenon to public attention. Nothing further seems to have resulted, however.

In 1884–1886, Sir Oliver Lodge brought up the subject in a series of articles, his researches and discoveries being made independently of the earlier investigations. The object he had in view was to use electrical discharges as a means for dissipating fog and smoke.

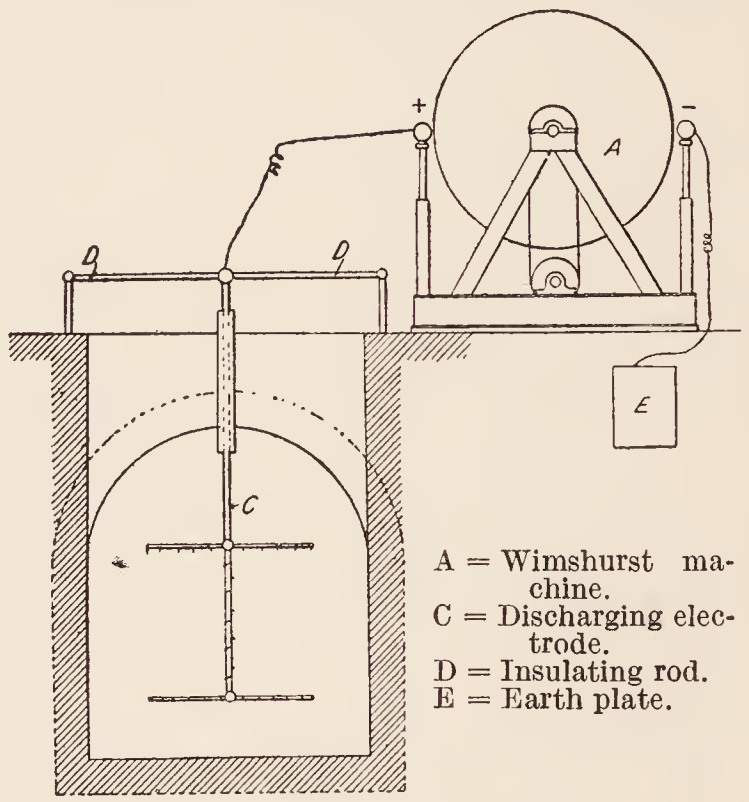
In 1885, A. O. Walker and W. M. Hutchings, in consultation with Sir Oliver Lodge, carried out a series of experiments on lead fumes at the Dee Bank Lead Works in Wales, but the means at their command of generating electricity were too inadequate to develop the system into a technical success, and the work was abandoned.

The method used was to subject the fume-laden gas in the brick flue from the lead furnaces to the discharge from a number of metallic points situated in the flue. These points were connected to the terminals of two Wimshurst machines, which had glass plates 5 feet in diameter and were driven by small steam engines. The arrangement is illustrated diagrammatically in Fig. 1.

These investigations led to the first patents being taken out in England and other countries in 1884 to 1886. During the same period, and quite independently, Dr. Carl Moeller, of Brackwede, Germany, experimented with the electrical precipitation of dust and fume, and obtained a patent in Germany in 1884. No commercial application, however, was made at the time.

During the following two decades very little was published beyond an occasional article calling attention to the possibilities of electrical precipitation, and a few patents taken out on minor details and modifications of what had gone before.

In 1906, Dr. F. G. Cottrell, who was then Professor of Physical Chemistry at the University of California, had occasion to repeat the earlier experiments of Lodge, while studying the problem of removing the acid mist occurring at certain stages in the contact sulphuric acid process. The method used by Cottrell of generating uni-directional high potential was to connect alternating current from an ordinary circuit to the primary windings of a step-up transformer and rectify the secondary high voltage current from the transformer by means of a rotating contact mounted on a small motor synchronously driven off the same supply as



A = Wimshurst machine.
C = Discharging electrode.
D = Insulating rod.
E = Earth plate.

FIG. 1.

fed to the primary terminals of the transformer. He soon became enthusiastic over the possibilities of electrical precipitation applied on a commercial scale, and subsequent tests made at the Hercules Works of the Du Pont de Nemours Company at Pinole, California, in 1906 demonstrated conclusively the practicability of the process.

The first commercial installation of any size was made at the plant of the Selby Smelting and Lead Company on San Francisco Bay for the collection of sulphuric acid fumes arising from 'parting kettles.'

It consisted briefly of a lead-lined flue of 4 feet by 4 feet area, in which were suspended, vertically and parallel to the sides of the flue, strips of lead 4 feet long by 4 inches wide leaving gaps 4 inches wide between them. In these gaps discharge electrodes were hung from horizontal bearers passing through the sides of the flue and resting on insulators placed outside. These discharge electrodes were built up of bits of mica or asbestos clamped between strips of hard lead, and they presented the projecting points to the earthed lead strips.

This first precipitator operated at a potential of about 17,000 volts and consumed 2 kw. per hour. It recovered sulphuric acid of sp.gr. 1·38 at the rate of 2 gallons a minute when the parting kettles were boiling briskly, and it provided the stimulus which led to a rapid development of electrical precipitation on a commercial scale.

Meanwhile, in England, electrical precipitation had been prosecuted independently by Sir Oliver Lodge and by his sons under the firm of the Lodge Fume Deposit Company. They subsequently pooled their experience with that of their American collaborators in the same field, as the result of which the firm of Lodge-Cottrell, Ltd., was formed.

Theoretical considerations.—To render air a conductor of electricity, the negative ions must be ejected from its molecules: it therefore requires to be subjected to ionisation, which can be brought about by various agents, such as radium, ultra-violet rays of a certain wave length, Röntgen and Becquerel rays, high temperatures, chemical reaction, and, finally, electrical discharge. The rays that effect ionisation lie in the extreme ultra-violet section of the spectrum, and the line of demarcation between the ionising and non-ionising portion is sharply defined, red rays, however powerful, not having the slightest influence on the conductivity of air.

Electrical precipitation on an immense scale occurs in nature, brought about by the electrical phenomena taking place in the atmosphere acting on the particles of dust and moisture suspended therein, but it is only during the last 7 or 8 years that reliable measurements have been taken of the amount of electricity passing with a flash of lightning and of the length of the disruptive discharge.

C. E. I. Wilson made a series of very valuable observations at Cambridge with the use of delicate instruments installed at two places a considerable distance apart. The charged thunder cloud produces at places in its neighbourhood certain electrical effects which are measureable, and the magnitude of which varies with the distance of the cloud and quality of the discharge taking place to earth. It was found that the average flash of lightning had a length of 10 km. and that the amount of electricity was equal to 30 coulombs. At the observation point the potential gradient was 2000 volts per metre, and it is safe to assume that in the direct line of actual discharge it was higher still. Taking the lower value, however, it follows that the actual difference of potential before the disruptive discharge occurred was no less than 20 million volts, and figuring on 30 coulombs, the energy liberated is equivalent to that of dropping a load of 600 tons through a distance of 100 metres. It is, furthermore, possible to calculate the expanse of the cloud required to accumulate the above charge, and this is found to be an area of one square kilometre. It is surprising, in view of the enormous amount of force involved, that the damage done is comparatively so small.

On the whole the passage of electricity through air is like that through electrolytes, though there are some fundamental differences. The wider the air gap separating two points of different potential, the greater the quantity of electricity passing, also the current does not increase in direct proportion with the voltage. This holds good within certain limits. When the two poles of a direct current source of supply are connected across an air gap the relation between current and potential will not follow Ohm's law; after a certain voltage has been reached no increase in current can be effected by raising the voltage. A point of saturation has been reached.

To explain the above, the ions present in the air gap must be regarded as the carriers of the electric current. The number of these present at any time limits the conductive capacity of the air gap, with the result that unless their number is increased by other means, no increase of current beyond a point corresponding to their carrying capacity can be brought about by raising the voltage. This holds good only up to a certain voltage, varying with the size of the air gap, above which the potential difference will set up ionisation of the gas, and the current will again increase as the voltage rises. The gas at this stage will become as good a conductor of electricity as a first-class electrolyte, *e.g.* dilute sulphuric acid, and this condition of high conductivity is a perfectly stable one, and no-wise comparable with a discharge from a Leyden jar. In electrical precipitation of liquids and solids from gases as developed technically, a strong electrical field is established between so-called receiving electrodes and discharge electrodes, which latter are connected to a suitable supply of high-tension voltage and are insulated, the receiving electrodes being connected to earth. The electrodes are shaped to meet the particular requirements, and may either be earthed plates opposed by charged wires between which the gas to be cleaned is led, or they may be earthed pipes with charged wires suspended in them, the gas travelling through the pipes and depositing the particles on the inside of the pipes.

The plate type of precipitator lends itself to numerous modifications of design. Thus the plate electrodes may be either plain plates or corrugated horizontally or vertically; sometimes they are provided with baffle ridges, or they may be constructed of wire screens. They may be placed parallel to the flow of, or across the path of, the gases to meet particular requirements. Likewise the discharge electrodes may be either wires or rods arranged horizontally or vertically, as the circumstances of the case may demand.

The passage of electric current through the gas separating the electrodes is influenced by the degree of ionisation of the gases. It has been found that gases derived from certain metallurgical operations are so highly ionised as to offer considerable difficulties to successful electrical precipitation. The air gap, so to speak, is short-circuited, and the potential difference that can be maintained without disruptive discharge does not suffice for establishing the required electrical field. Means have been suggested for de-ionising the gas by attaching the ions to slow-moving carriers, or by bringing about a recombination of the negative and positive ions in various ways. On the other hand, electrical precipitation is impossible to carry on successfully without the help of the stream of ions

sent out by the discharge electrode, and the shape and dimensions of the latter has a very material effect on the ionisation, and must be carefully adapted to suit the conditions encountered. What may answer for one gas and for one temperature may be useless for others. Another condition for successful precipitation is that the earthed electrode and its deposit shall be maintained at zero potential. If this is not done peculiar electrical disturbances take place.

Commercial installations.—The first electrical plant of any size in this country was erected for the Ministry of Munitions at Queen's Ferry in connection with the Gaillard sulphuric acid concentrating towers, in which the spent acid from the T.N.T. factory was brought up to strength.

The installation with all four compartments working was designed to take a total of 64,000 cub. ft. of gas per minute at a temperature of 80°C., and carrying about 4 grains of SO_3 per cub. foot. Two flues, one from each battery of eight Gaillard towers, joined into a common flue conveying the gases to the precipitating chambers (*see* Fig. 2) built side by side with a common connecting flue at each end. Each chamber was 30 feet long, 7 feet 6 inches wide, and 8 feet 6 inches high, and was built on a bed of concrete raised sufficiently above ground level to allow the precipitated acid to drain into tanks.

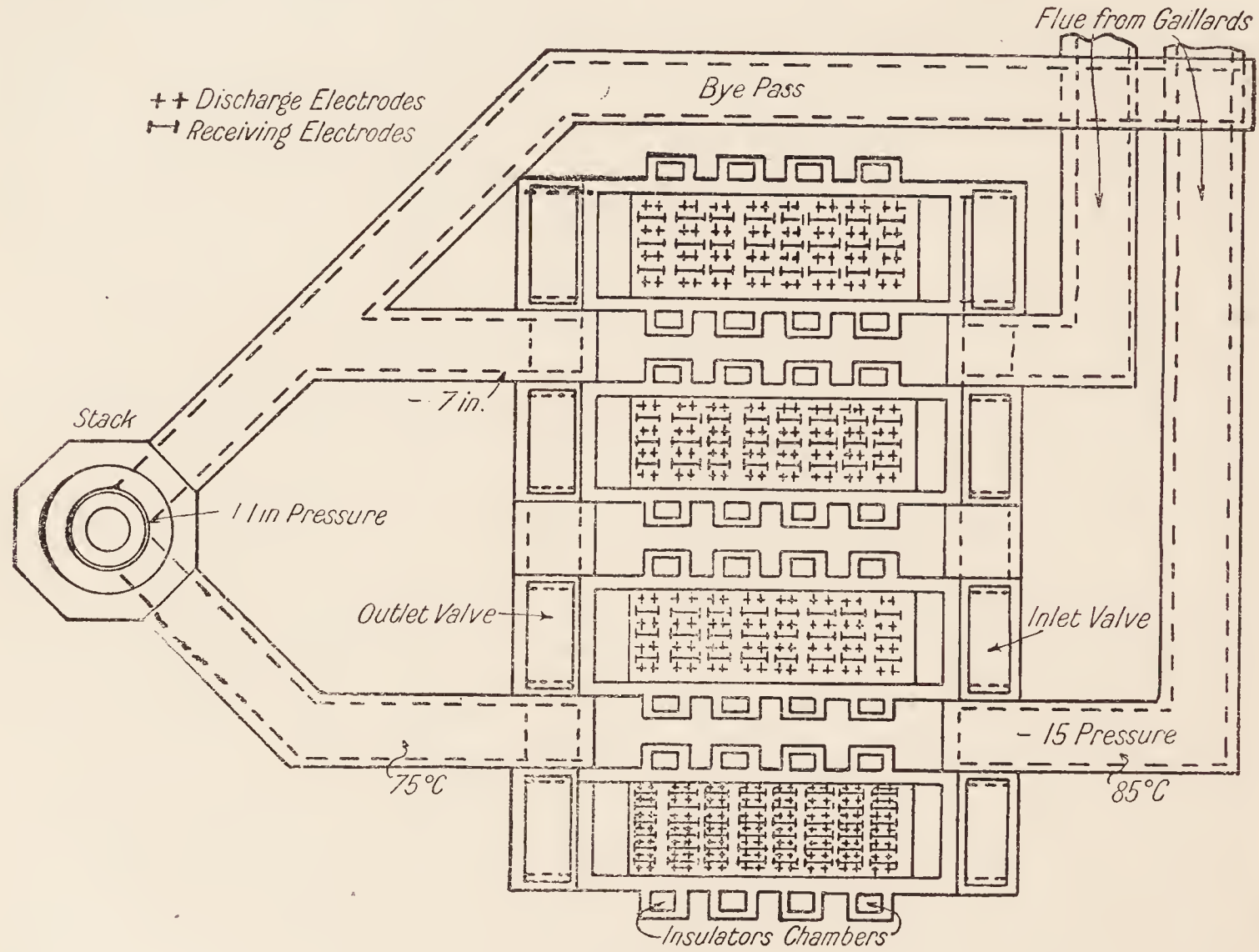


FIG. 2.

The dishes and walls of the chambers were built of acid-resisting brick set in special cement, the dishes having a lining of 8-lb. lead flanged over and built into the walls.

The top of the precipitator was formed with luted lead-lined wooden covers (Fig. 3).

Lead sheets 8 feet 6 inches by 2 feet, weighing 8 lbs. to the square foot, formed the receiving electrodes, they were carried from lead-covered M.S. bars and hung 10 inches apart. Between them were suspended vertically from lead-covered longitudinal bearers rows of discharge electrodes. These were extended rods of regulus metal 7 feet long, having a cruciform cross-section with two long and two short members. The former were one inch long and had sharp edges facing the receiving electrodes. The regulus rods were burned to lead-covered M.S. bars carried in turn by transverse lead-covered M.S. bars. These passed through openings in the side walls of the chamber and were fixed to channel stancheons mounted on porcelain insulators. The latter and the stancheons were encased in narrow brick chambers fitted with inspection doors and slides to regulate the small amount of air intentionally drawn in around the insulators.

There were 144 discharge elctrodes and 64 receiving electrodes to each chamber.

The high tension uni-directional current was obtained by connecting one phase of the work's alternating current supply at 440 volts through a contact panel to the primary of a step-up transformer, ratio 440/85,000, the secondary terminals of which were connected to two poles of a mechanical potential rectifier of the disc type. The disc of insulating material was mounted on the extended shaft of a small synchronous motor driven off the same 440 volts supply, and was fitted with two metallic

strips, which formed the contacts revolving in synchronism with the alternations of the primary circuit of the transformer. The third contact of the rectifier was joined to the conductor carrying the high tension current to the busbars in the precipitating chambers, a special leading-in insulator being used where the conductor passed through the wall. One of the latest types

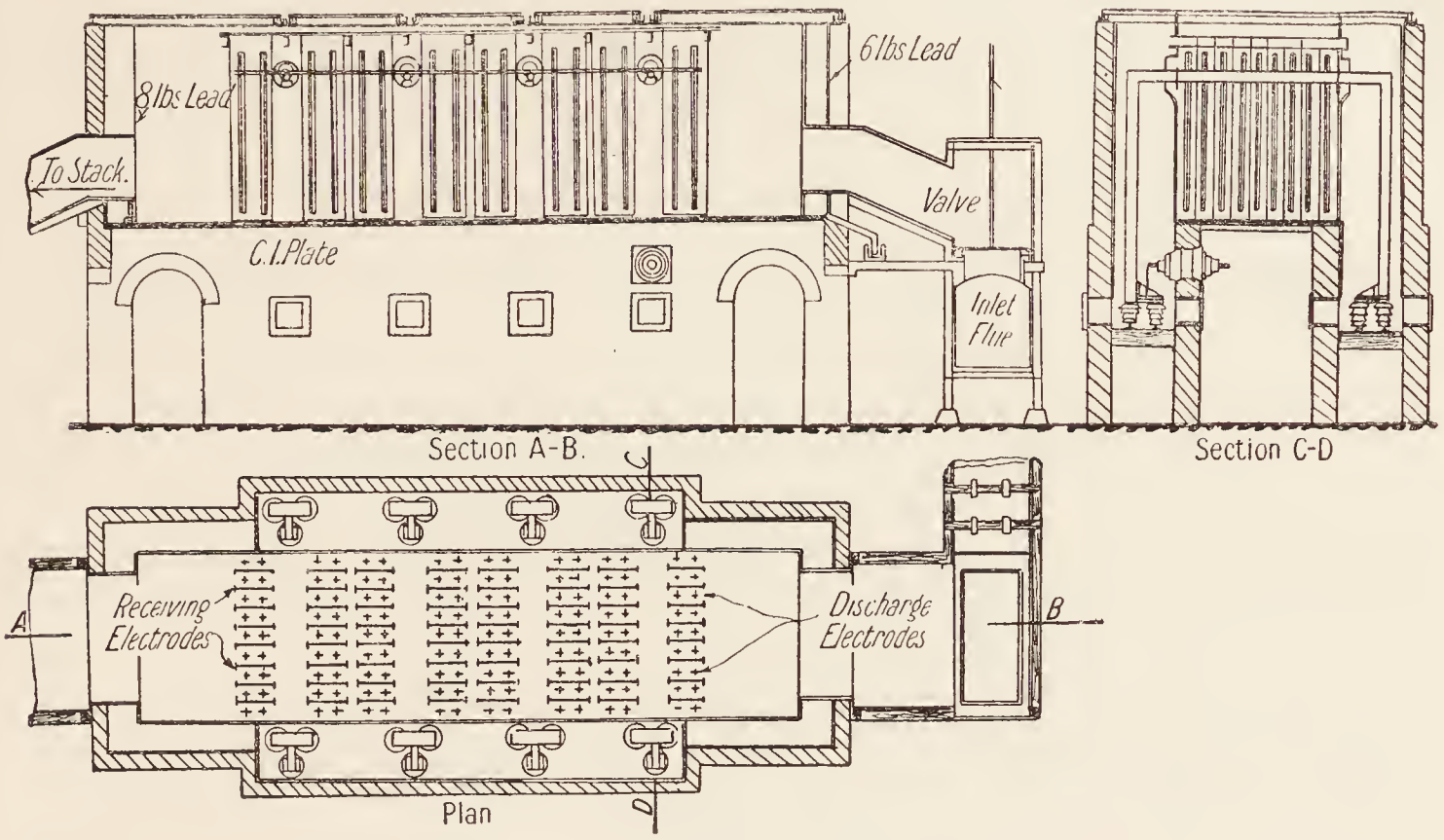


Fig. 3.

of rectifier direct-coupled to a synchronous motor is shown in Fig. 4.

From the earthed receiving electrodes a return wire was run back to the fourth pole of the rectifier. The control panel in the primary circuit of the transformer included besides automatic circuit-breaker, ammeter, voltmeter, grid resistance, and double-pole double-throw switch, a dial switch with 18 points, by

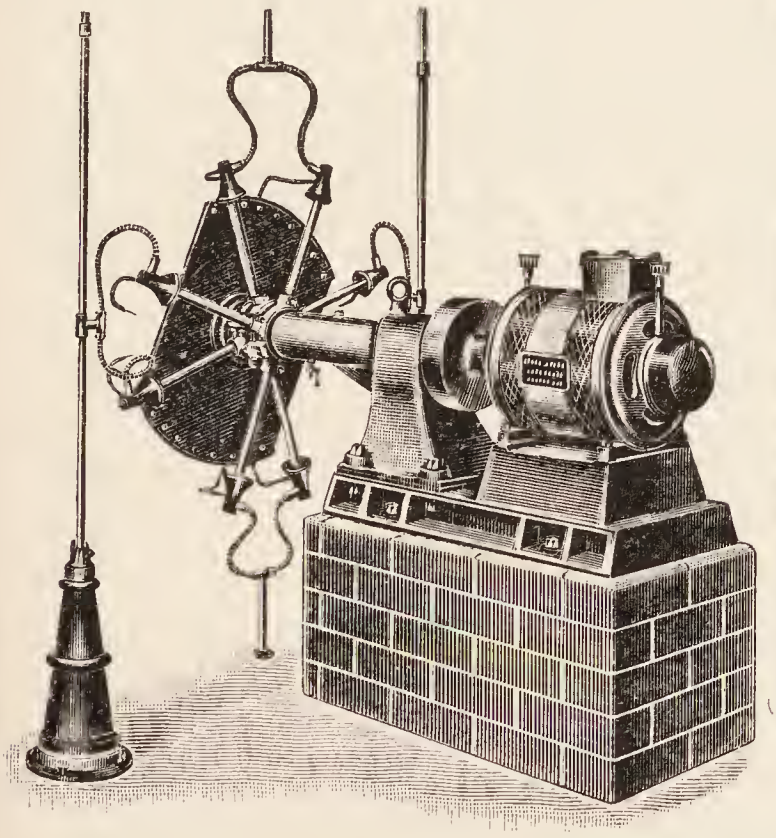


Fig. 4.

means of which through an auto-transformer the voltage of the step-up transformer could be adjusted to give a secondary varying between 35,000 and 85,000 volts.

There was one such generating set for each chamber and a spare set ready for switching on to any of the four in case of emergency. The average operating voltage was 73,000 and the current consumption per chamber 155 kw. hours per day.

In this plant from 25 to 30 tons of sulphuric acid were recovered per day, containing 50 p.c. of mono-hydrate. It is interesting to note that at times appreciable quantities of dinitrotoluol were precipitated as well, especially when the temperature in the chambers was allowed to fall below 50°C.

At the Royal Naval Cordite Factory, Holton Heath, a slightly different design was used for treating the exit gases from a battery of Kessler sulphuric acid concentrators. Alternate units of existing scrubbers were converted into electrical precipitators by emptying the packing and using the lead-lined shells as boxes, into which to hang the opposing electrode batteries of similar design as those used at Queen's Ferry. The transverse horizontal bearers carrying the discharge electrodes were in this case suspended from insulators placed in boxes above and outside the stream of mist-laden gases. The waste gases from two Kesslers were exhausted through one packed scrubber by means of a high-pressure Kestner fan and blown through two precipitating chambers in parallel arranged inside the converted scrubber. A second fan exhausted the clean gas from the chambers and delivered it into the exit stack. Luted covers on top of the chambers facilitated the erection and the inspection of the electrode batteries.

The same system as at Queen's Ferry was used for supplying the high-tension uni-directional current. The operating voltage was 55,000 and the current through a twin set was less than 5 amperes.

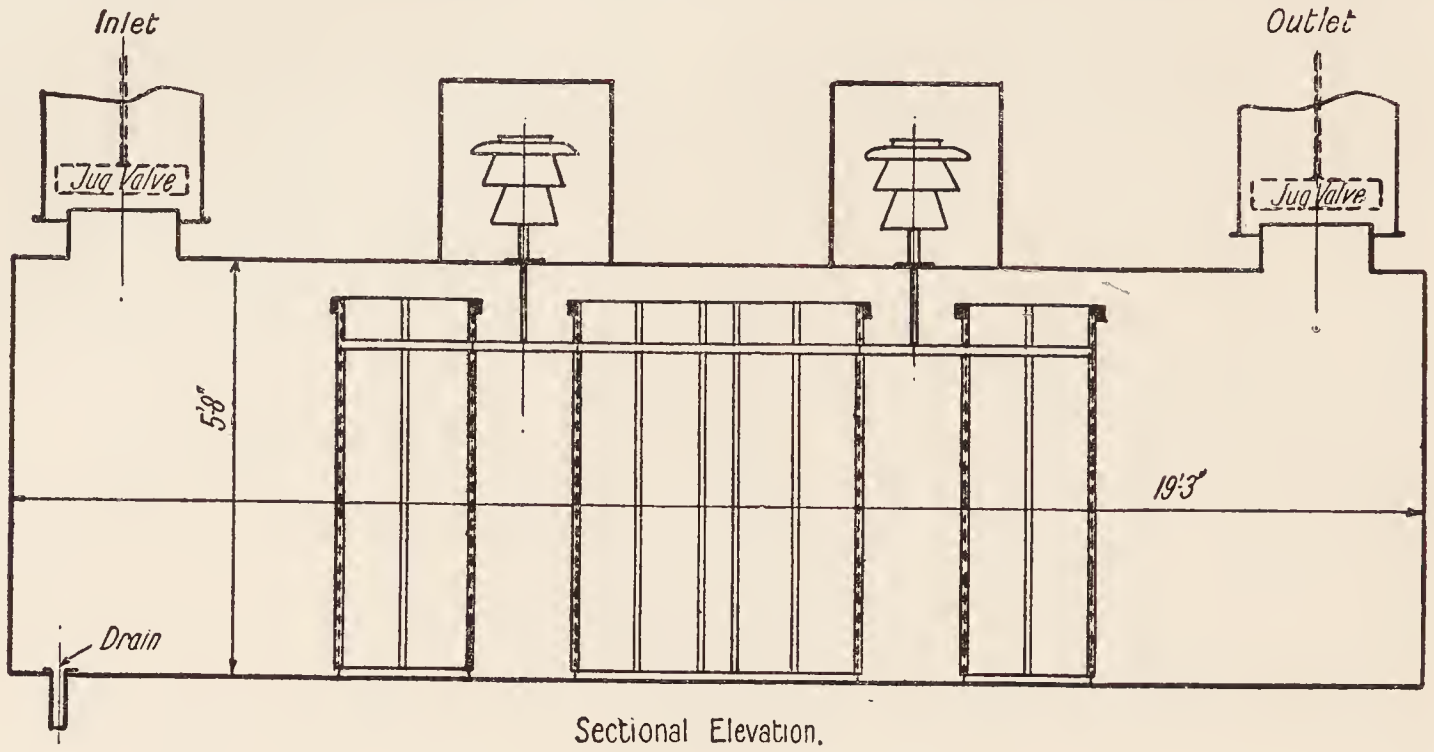
The conductor from the rectifier to the precipitators was carried on tall poles fitted with insulators and throw-over switches, so arranged that any one chamber could be isolated without interfering with the remainder.

The temperature of the gases entering the chambers was 51°C., and the acid recovered showed an average contents of 33 p.c. by weight of mono-hydrate.

Fig. 5 shows a longitudinal section through one chamber.

Fig. 6 is a plan of the grouping of the electrodes.

The installations so far mentioned are of the



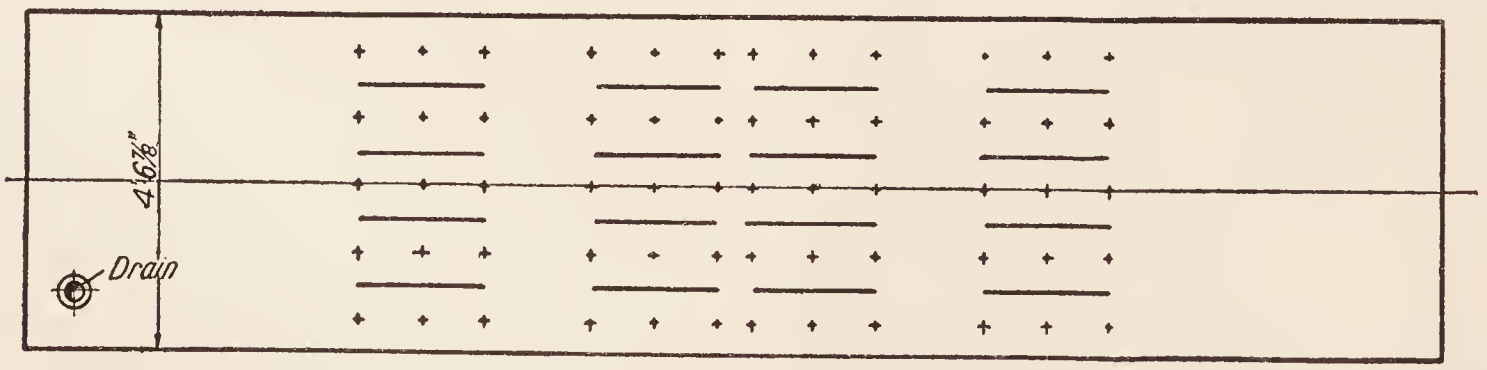
Sectional Elevation.

FIG. 5.

plate-and-rod type. Fig. 7 shows a small pipe-and-wire design erected at a metallurgical works for the recovery of very fine precious metal dust. The dust-laden gases after entering a distributing chamber are passed downwards through a number of vertical steel sheet pipes arranged in units of four. On leaving the pipes the clean gases rise upwards round the outside and enter a common flue at a level just below the top of the pipes. The pipes are supported in a steel framework of angles and tees covered in with asbestos cement sheeting. A number of pendulum hammers are arranged on horizontal shafts for jarring the pipes to dislodge the dust deposited on the inner surface. The steel framework and pipes are maintained at earth potential. From busbars carried on special porcelain insulators an iron wire is suspended in the centre of each pipe with a weight attached at the end to keep it taut. A steel frame fixed to insulators in the bottom header prevents the wires from oscillating and getting out of centre. By means of a hand-operated hammer, which strikes an anvil mounted firmly on the busbar, the discharge wires can be agitated periodically in order to remove any adhering dust.

The recovered dust, being of considerable value, is removed from the lower chamber by means of hand brushes and collected in leather bags.

The high-tension conductor from the potential rectifier is passed through a leading-in insulator fixed in the floor of the top distributing chamber and securely connected to the busbars. At these works only direct current was available,



Plan showing arrangement of electrodes

FIG. 6.

and the high-tension electrical generating set is somewhat different from the previously described one. It comprises a direct-current motor driven off the works supply coupled to a single-phase alternator, which receives its excitation from the same supply. On the extended shaft of the alternator is mounted a disc revolving in sychronism with the alternations of the current supplied by the alternator to the primary of the transformer.

The secondary voltage of the transformer can in this case be adjusted to the desired value by means of a regulating resistance in the field circuit of the alternator. In the primary

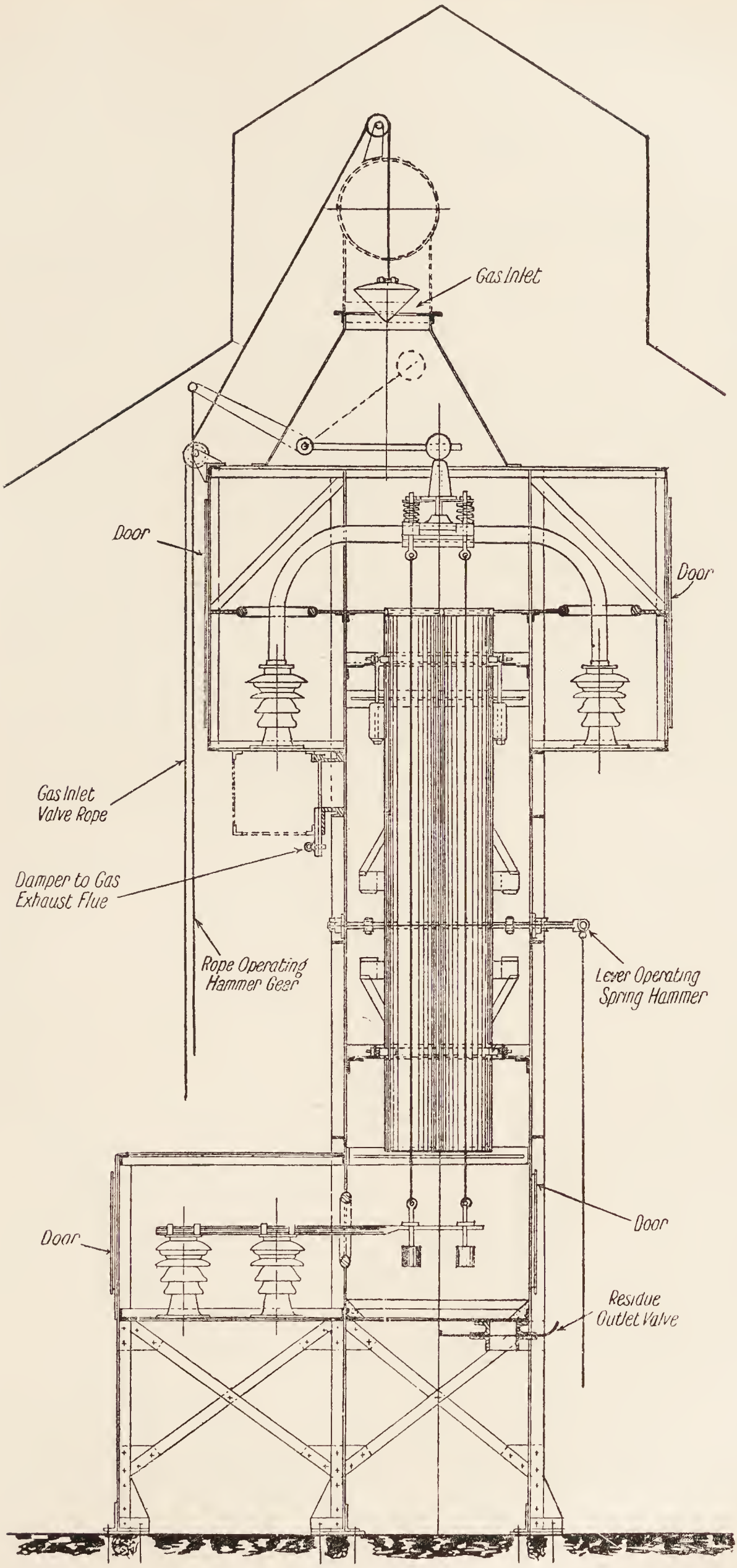

Gas Inlet
Door
Door
Gas Inlet Valve Rope
Damper to Gas Exhaust Flue
Rope Operating Hammer Gear
Lever Operating Spring Hammer
Door
Door
Residue Outlet Valve

FIG. 7.

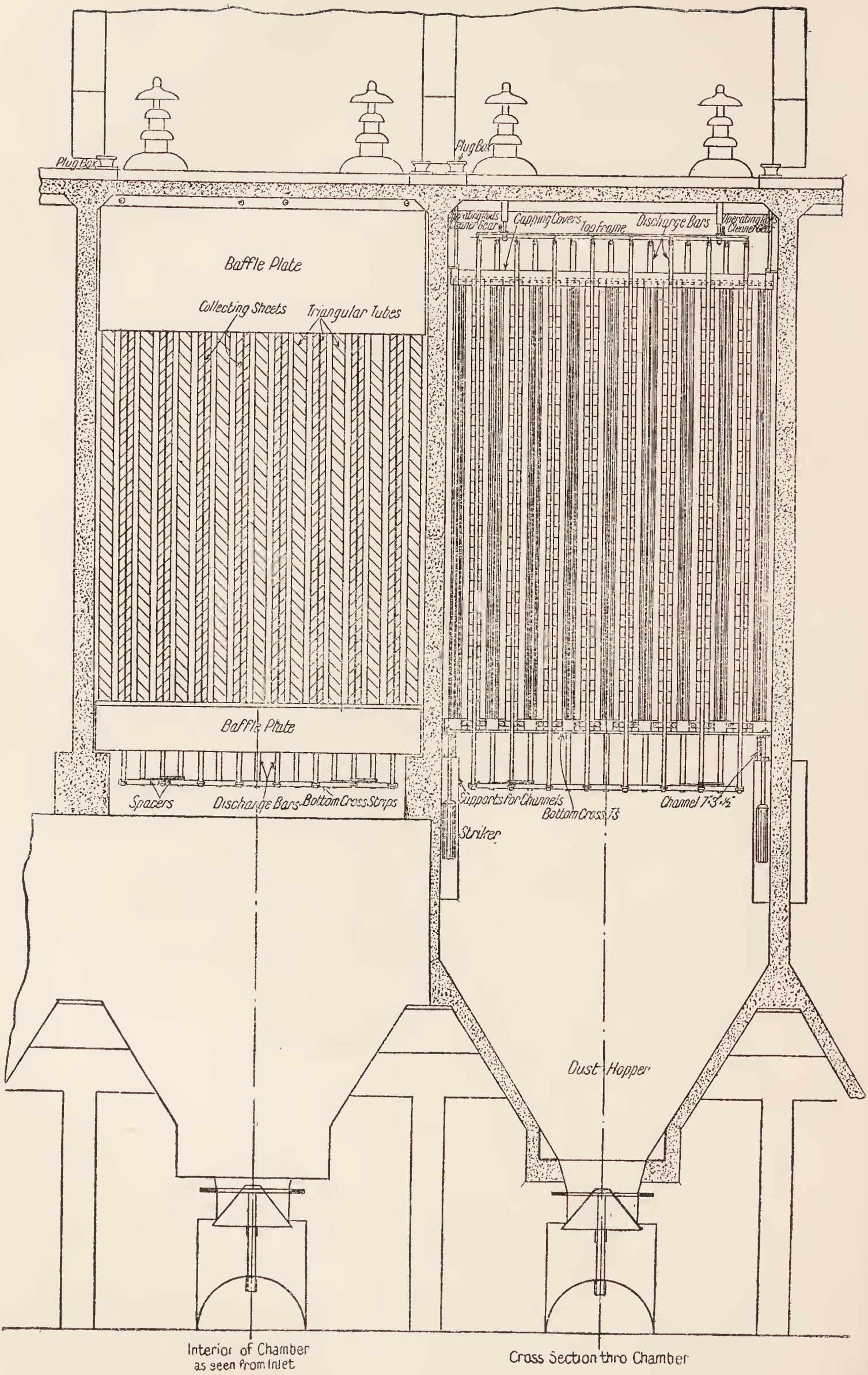

Plug Box
Plug Box
Baffle Plate
Collecting Sheets
Triangular Tubes
Capping Covers
Top Frame
Discharge Bars
Baffle Plate
Spacers
Discharge Bars
Bottom Cross Strips
Supports for Channels
Bottom Cross Ts
Channel 7"3·½"
Striker
Dust Hopper
Interior of Chamber as seen from Inlet
Cross Section thro Chamber

FIG. 8.

circuit the usual measuring instruments are arranged as well as the automatic circuit breaker, fuses, grid resistances, and double-pole double-throw switch, which allows either polarity to be impressed upon the contact of the rectifier connecting to the precipitator.

It is interesting to note that the refining process adopted at this plant depended for its success on a fume recovery plant, the conditions attached to which could only be met by electrical precipitation. Not only was the gas evolved highly corrosive when wet, but the constituents of the fume when moist decomposed in contact with metalwork and rapidly corroded it. This was entirely overcome by treating the gases hot in the electrical field. The recovery has proved practically complete.

The choice between synchronous motor and motor-alternator depends upon local conditions to some extent, as well as on consideration of cost. If a steady and ample supply of alternating current is available, synchronous motors can be used with advantage; if the supply is fluctuating or only direct-current is available, motor generators are called for. Special precautions must be taken to protect these machines from the oscillations and surges that may be set up in the circuit, and which may reach considerable magnitudes.

For cleaning the gases from blast-furnaces both the plate and the pipe-type of electrical precipitator have been used.

The gases have an average calorific value of 100 B.Th.U. per cub. foot, and constitute a valuable form of fuel for heating Cowper stoves, furnaces, and boilers; they are also used, sometimes enriched with coke-oven gas, for driving gas engines. Their dust contents varies up to 15 grms. per cub. metre, 5 grms. being an average figure.

Fig. 8 and Fig. 9 show respectively a sectional elevation and plan of the plate-and-rod precipitator erected at the works of the Skinningrove Iron Company, Ltd., for treating the gas from 4 blast-furnaces producing basic pig. The installation consists of 16 compartments built in ferro-concrete side by side, each with its own inlet and outlet valve. The receiving or depositing electrodes are thin sheet steel plates 18 inches wide by 10 feet long resting on steel supports, and arranged parallel to the flow of the gases. Between the plates from a steel frame suspended from special insulators are hung vertical rods having short horizontal cross-pieces arranged at intervals, which project towards the plates, there being 14,000 such discharge points to each compartment. An ingenious rapping device operated by hand from the top of the chambers jars simultaneously the steel grid supporting the receiving electrodes and the frame from which the discharge members are suspended.

The rated capacity of one compartment is 10,000 cub. feet of gas per min. measured at operating temperature.

It will be noted (Fig. 10) that the electrical generating set is arranged above the chambers, which makes the whole installation self-contained and compact. The generating system for supplying the high-tension current is of a special kind, and differs appreciably from the method described above.

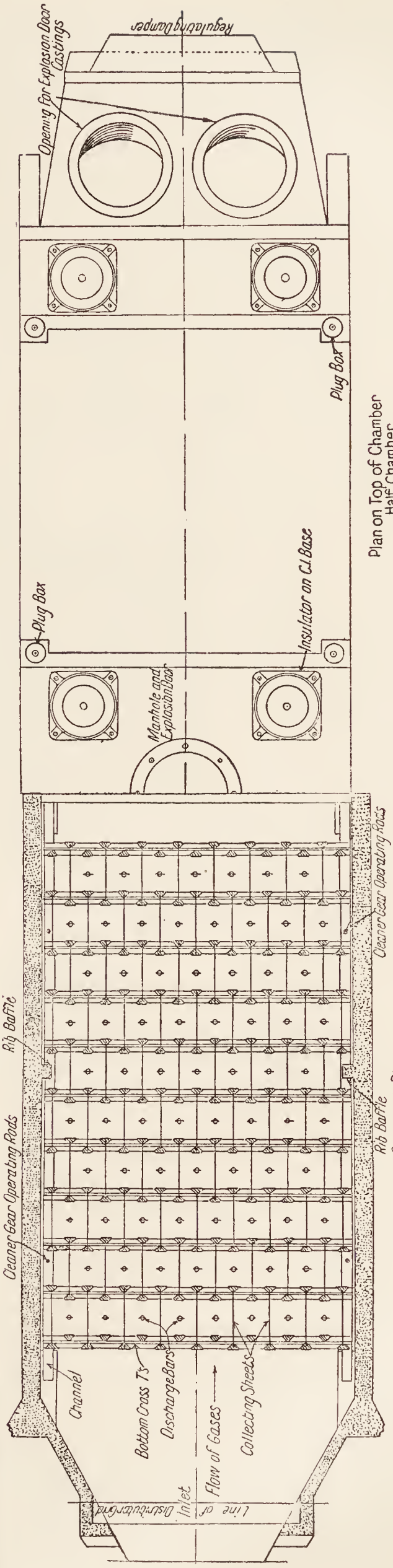


FIG. 9.

A pipe-and-wire type of electrical precipitator is installed at the blast-furnace plant of the Workington Branch of the United Steel Companies. It consists of six units of 64 pipes each, 9 inches in diameter by 12 feet long, arranged between top and bottom headers which connect with the dirty gas and clean gas main respectively. The top headers are built of brick and house the inlet valves, distributing chamber, bus-bars carrying the discharge wires, rapping

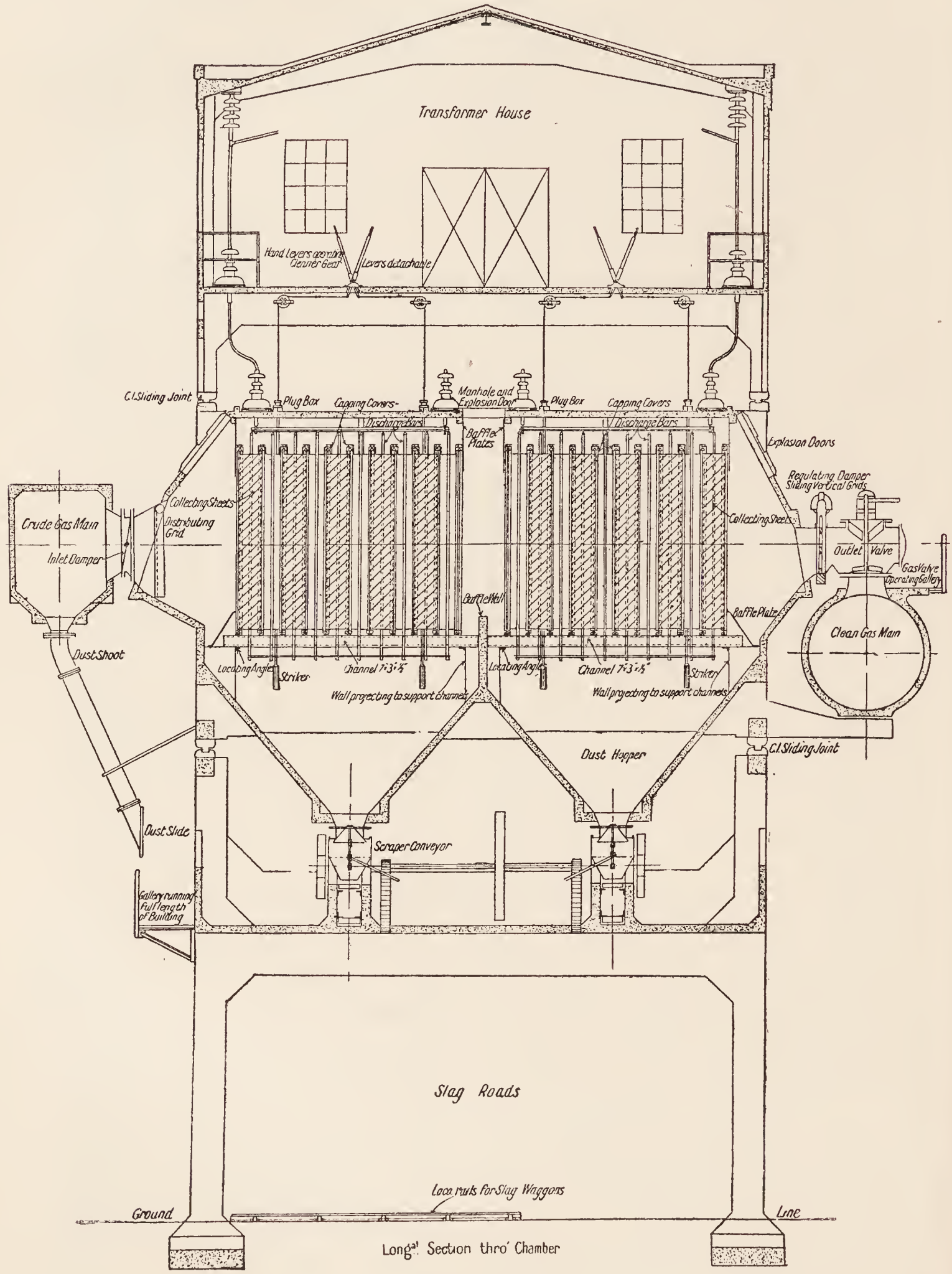
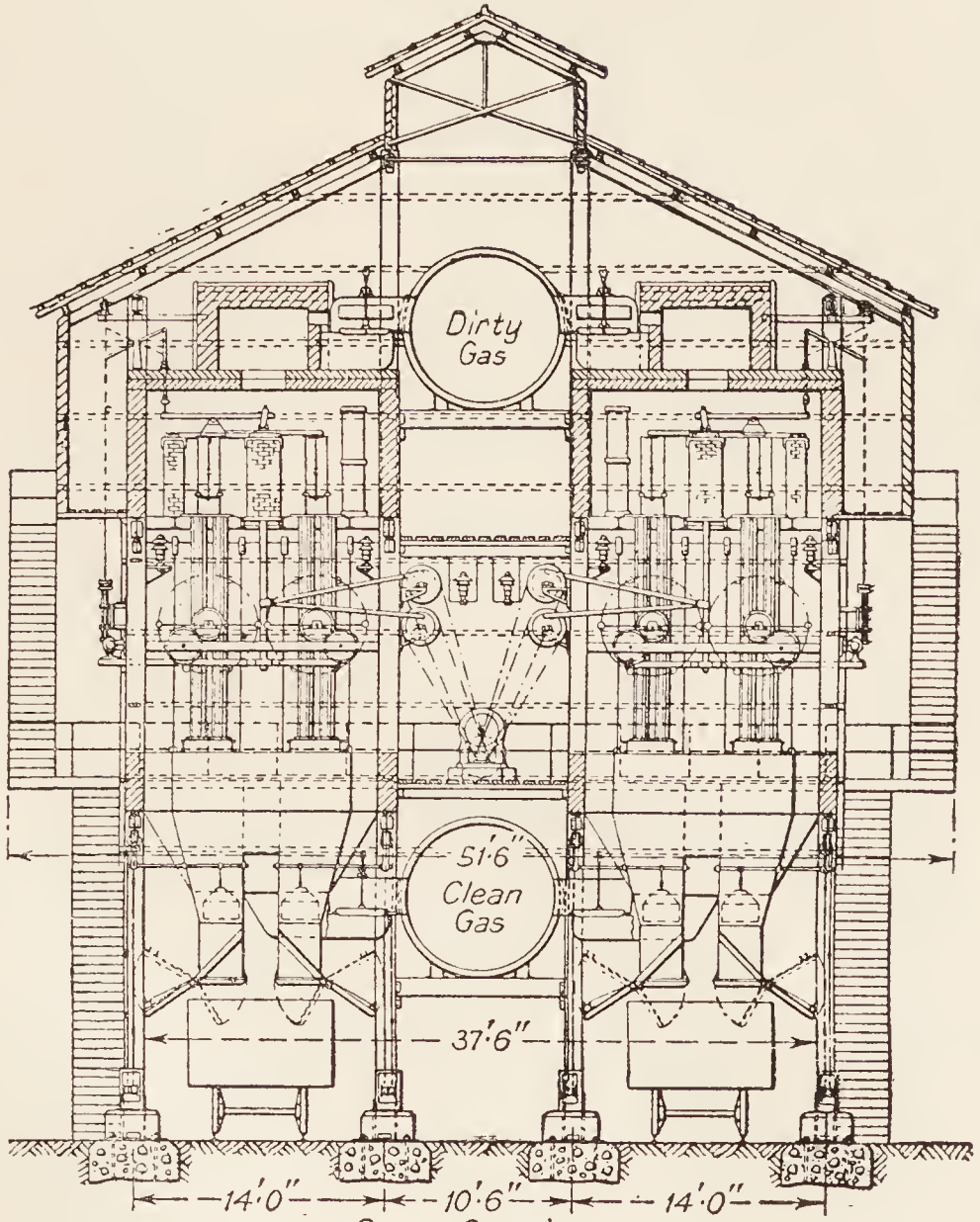


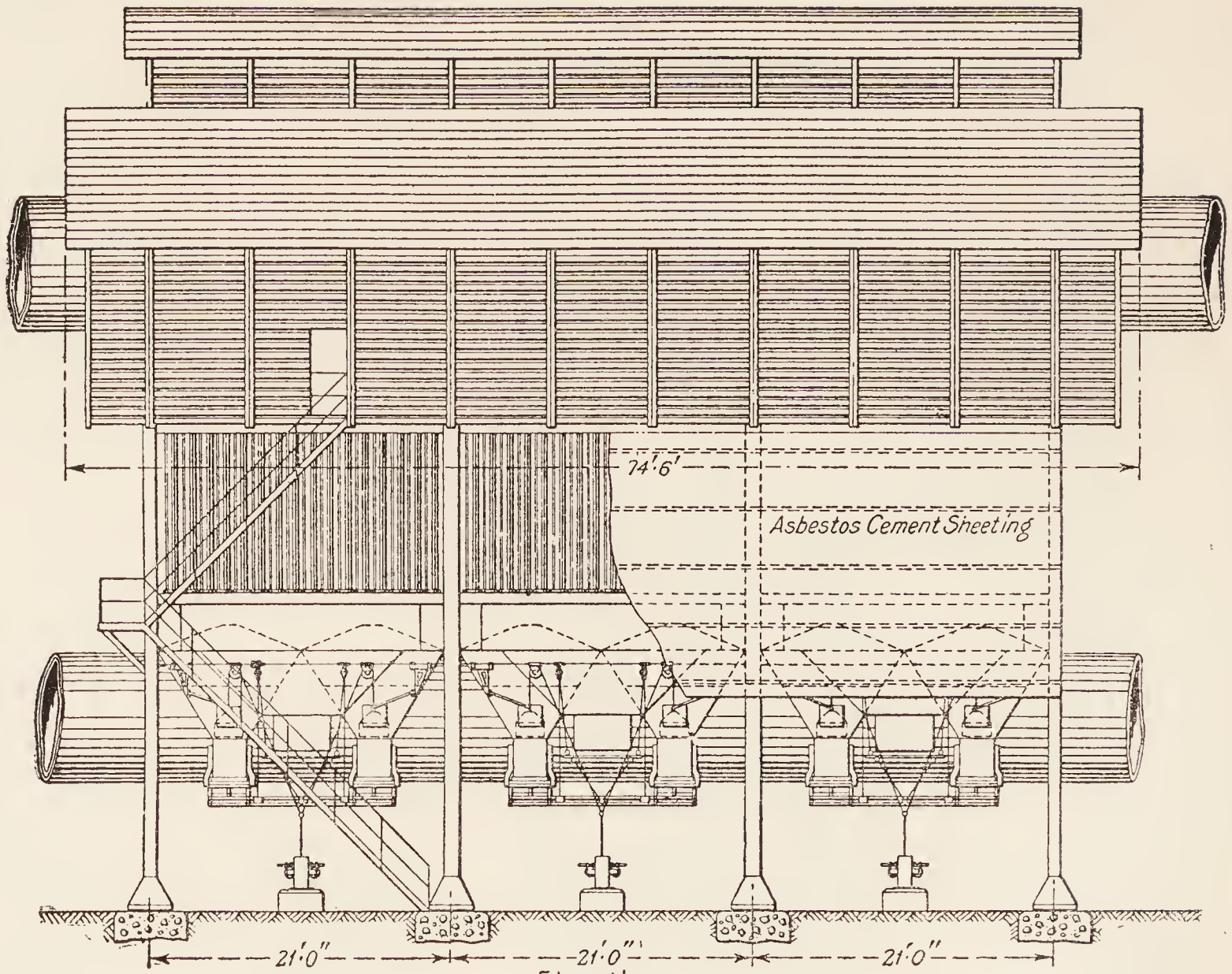
FIG. 10.

gear for same, and leading-in insulators for bringing in the high-tension lead from the potential rectifier. The bottom headers were fitted with steadying grids for the discharge wires, outlet valves, and steel hoppers, with suitable devices for discharging the precipitated dust into railway trucks. By means of pendulum hammers operated from a motor-driven counter-shaft the pipes can be hammered on the outside to dislodge the dust accumulated on



Cross Section.

From 'The Electrician.'] FIG. 11.



Elevation.

FIG. 12.

the inside. The rapping gear for the discharge wires is actuated from the same mechanism. Each unit of 64 pipes is self-contained, and has its separate high-tension lead from a 25 K.V.A. generating set, comprising motor-generator, control panel, transformer, potential rectifier, and isolating switch.

The six electrical units are so arranged that either one can be switched on to any one precipitating chamber, or one unit may be made

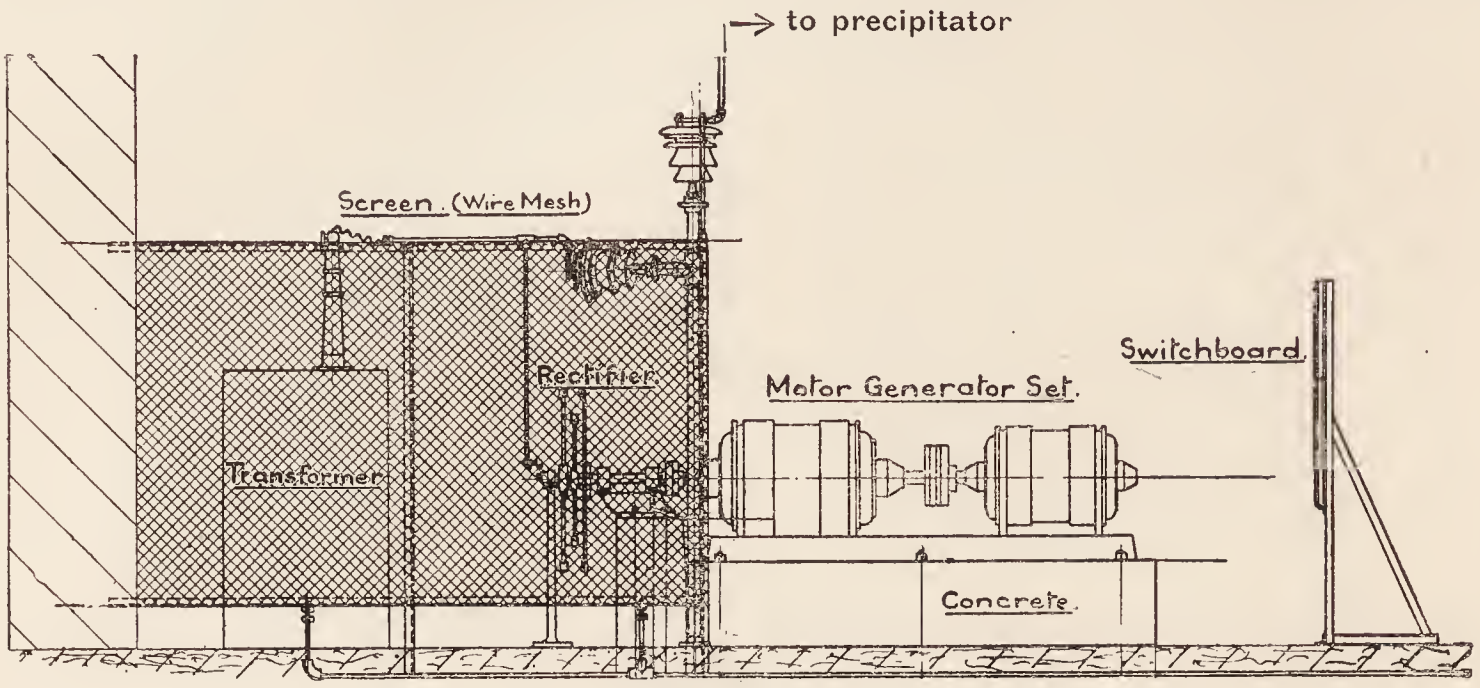


Fig. 13.

to serve more than one set of pipes as circumstances may demand.

Fig. 11 is a sectional elevation of the precipitator.

Fig. 12 is a side elevation of the same.

Fig. 13 shows the arrangement of the electrical generating set in what is termed the rectifier house.

The rated capacity of each compartment is 10,000 cub. feet of gas per minute; the gases entering have a temperature of 225° to 250°C. The operating voltage on this installation is about 50,000 volts and the total power consumption 25 kw. per hour. With two furnaces turning out 800 tons of hematite each per week an average of 5½ tons of dust is collected per 24 hours.

Extensive use has been made of electrical precipitation in the United States for combating the dust nuisance arising from the waste gases of rotary cement kilns. In the 'dry' method which predominates in that country an amount of fine material is carried away by the combustion gases amounting to 5 p.c. of the raw mix fed into the kilns. The classical example in this field is the installation built for the Riverside Portland Cement Company, of Riverside, California. The increasing claims on behalf of the orange and lemon growers for alleged damage to their crops by the dust emitted from stacks of 10 rotary kilns led to the first electrical precipitating installation of this kind being put down in 1912. It was a plate-and-wire system designed to deal with nearly one million cub. feet of gas per minute.

Fig. 14 shows the type of receiving electrode employed—a wire screen in angle framework. The gases from the kilns were taken through short connecting flues straight into the precipitating chambers, the temperature rising occasionally to over 400°C.

The weight of dust collected in this installation amounts to over 90 tons in 24 hours, containing an appreciable percentage of potash. It finds a ready sale amongst the local farmers, and the revenue derived therefrom has enabled the company to write off the complete cost of the electrical precipitators in the course of a few years. Thus what was formerly a cause of unending anxiety and very nearly led to a legal

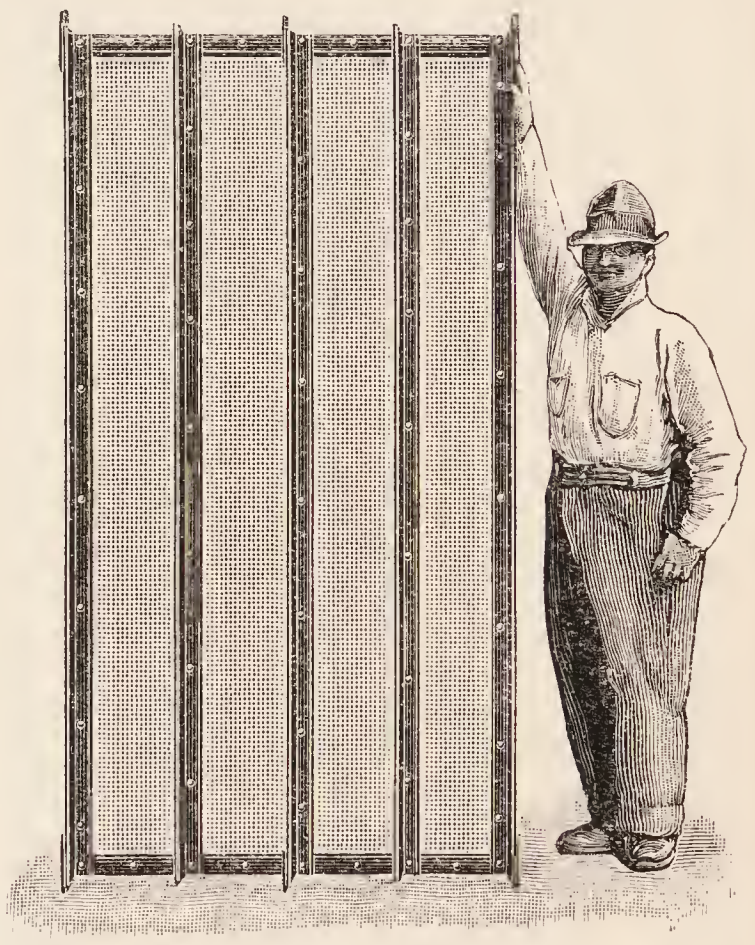


Fig. 14.

injunction to close down the manufacture now constitutes a useful source of revenue.

A marked advance in precipitation of cement kiln dust is represented by the plant erected by the Santa Cruz Portland Cement Company, of Davenport, California. This type is illustrated in Figs. 15 and 16 in plan and elevation.

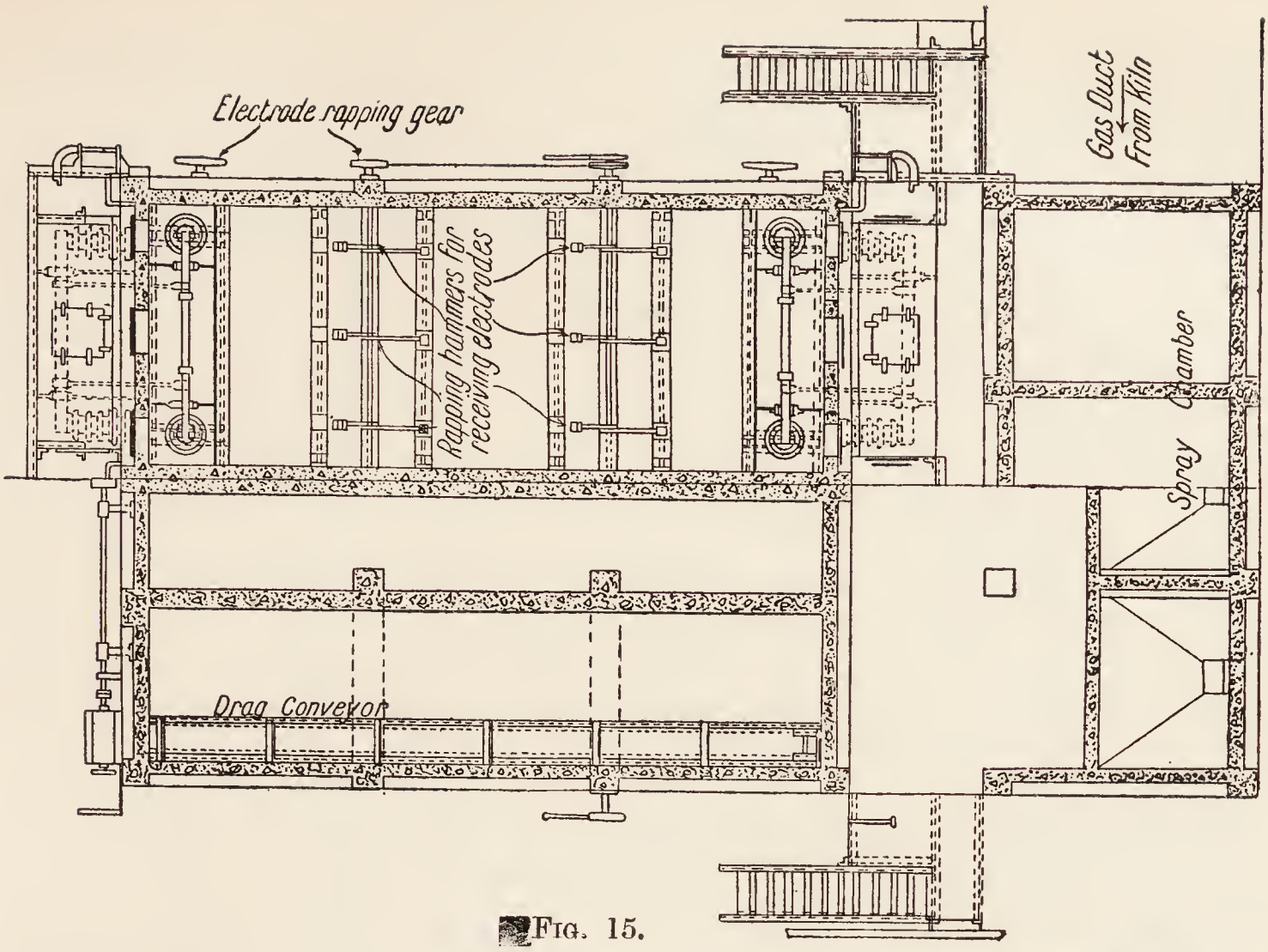

Electrode rapping gear
Gas Duct
From Kiln
Rapping hammers for
receiving electrodes
Spray Chamber
Drag Conveyor

FIG. 15.

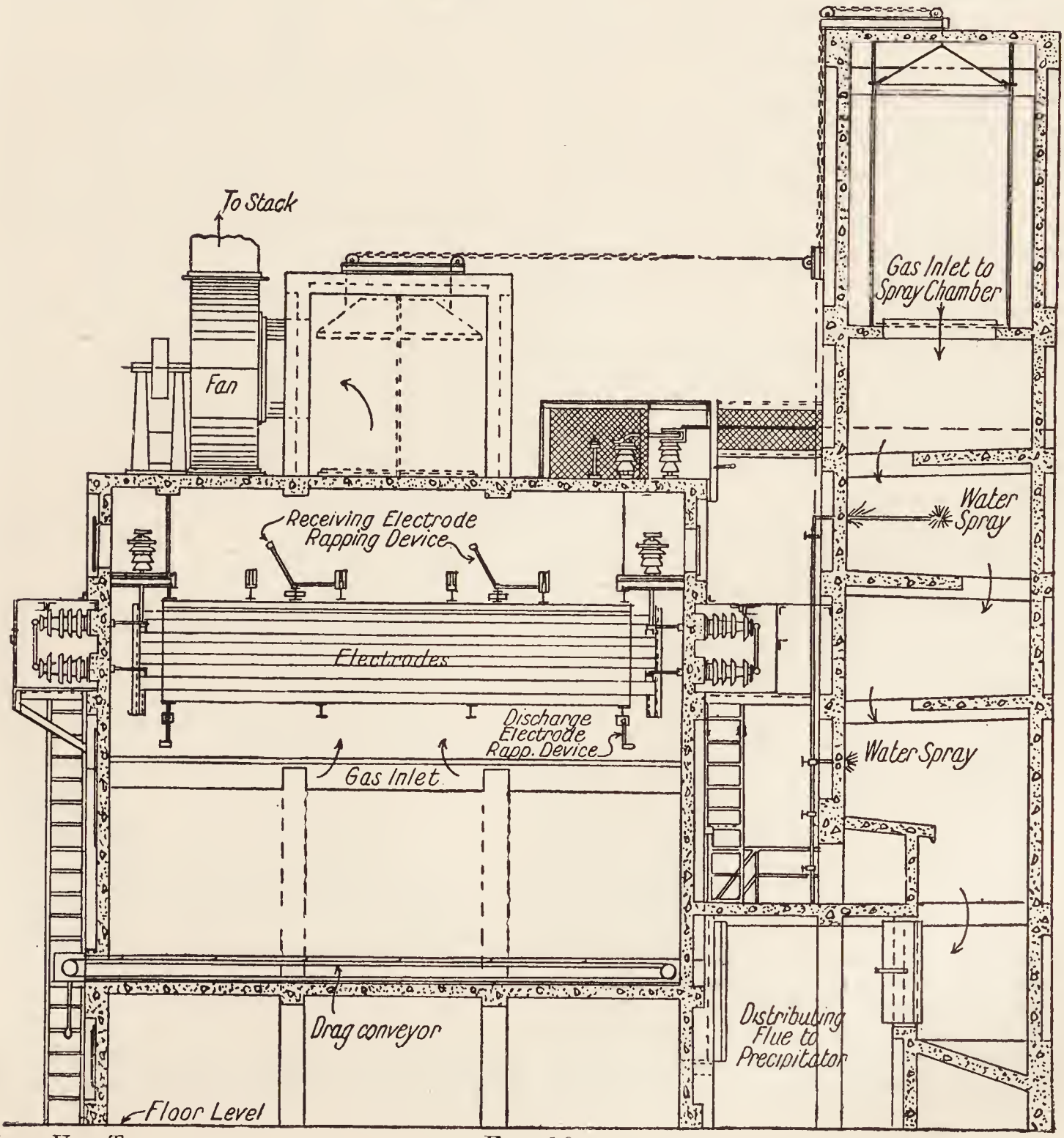

To Stack
Gas Inlet to
Spray Chamber
Fan
Water
Spray
Receiving Electrode
Rapping Device
Electrodes
Discharge
Electrode
Rapp. Device
Water Spray
Gas Inlet
Drag conveyor
Distributing
Flue to
Precipitator
Floor Level

FIG. 16.

The dust from the kilns containing considerable quantities of potash, a combination of water spraying and electrical precipitation has been resorted to with the object of separating the coarse dust, which contains little potash, from the very fine fume containing most of the alkali volatilsed in the burning process.

The raw materials used are limestone and clay, which are mixed and burnt in the manner usual in the 'dry' process. The raw mix as fed to the kilns is ground to such a degree of fineness that 90 p.c. of it will pass through a 200 mesh screen, and it contains on an average 0·83 p.c. of K_2O. The burnt clinker contains 0·54 p.c. of K_2O, and the amount of potash volatilised is practically two pounds of K_2O per barrel (380 lbs.) of clinker.

The dust-laden gases emerge from the kilns at a temperature of 1400°F., and are passed through a brick-lined steel flue to a spray tower built of concrete 6 feet by 10 feet by 21 feet high. Inside the tower are arranged a number of shelves or baffles at a slight inclination to the horizontal, and a system of sprays on the top supplies the necessary water.

The amount of water must be adjusted to bring down the coarse dust without causing the potash salts to be precipitated in a moist condition in the subsequent stage. About 75 gals. of water per minute are needed per kiln. The slurry running off from the spray tower is concentrated in Dorr thickeners, filtered, and returned to the kilns for burning.

The gases, reduced in the spray tower to a temperature of about 212°F., pass on to the electrical precipitator, a concrete chamber 34 feet long by 13 feet wide, in which are suspended corrugated sheets as depositing electrodes six inches apart. Between the plates horizontal wires are passed and held in position by two vertical frames attached to porcelain high-tension insulators.

The potash salts show a tendency to deposit irregularly on these wires, and means are provided for dislodging them by rapping the insulated frames through which the wires are threaded. The deposit of salts on the plates drops off by itself when it has reached a certain thickness.

The salts as discharged from the precipitator by the scraper conveyor are white and very light. To facilitate packing they are passed between slow-moving rolls, which increases their weight per cubic foot fourfold.

From 2000 lbs. to 2400 lbs. of salts are recovered per kiln in 24 hours of a fairly uniform composition.

K_2O . . .	32·59 p.c.
Na_2O	8·36 ,,
Insoluble . . .	5·22 ,,
SO_3	40·19 ,,
Cl	0·49 ,,
CaO	10·79 ,,
H_2O	0·49 ,,
Co_2, &c., by difference .	1·87 ,,

A further development of this method of fractional precipitation is shown in Fig. 17. The relatively coarse cement dust as distinct from the volatilised potash fume is electrically precipitated in the first stage, consisting of a ferro-concrete chamber with plate receiving electrodes and horizontal wire dischargers. The

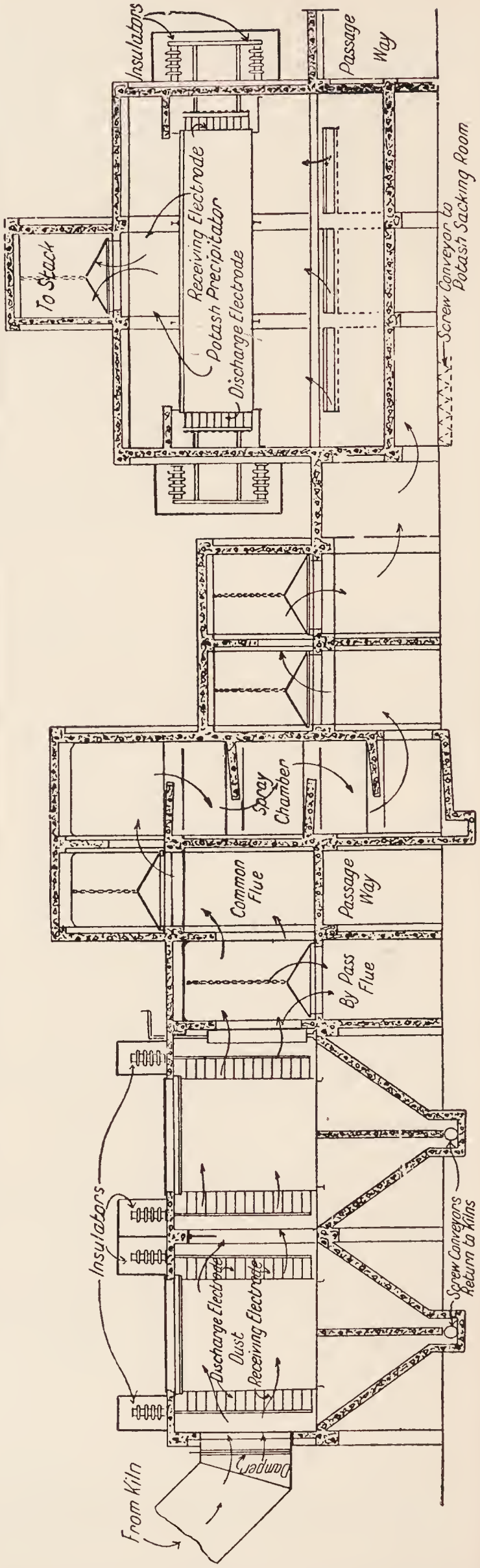


FIG. 17.

gases then pass through a spraying tower, where they are cooled and supplied with enough

moisture so that they enter the second stage of electrical precipitation in a favourable condition for separating out a dry material containing a high percentage of potash.

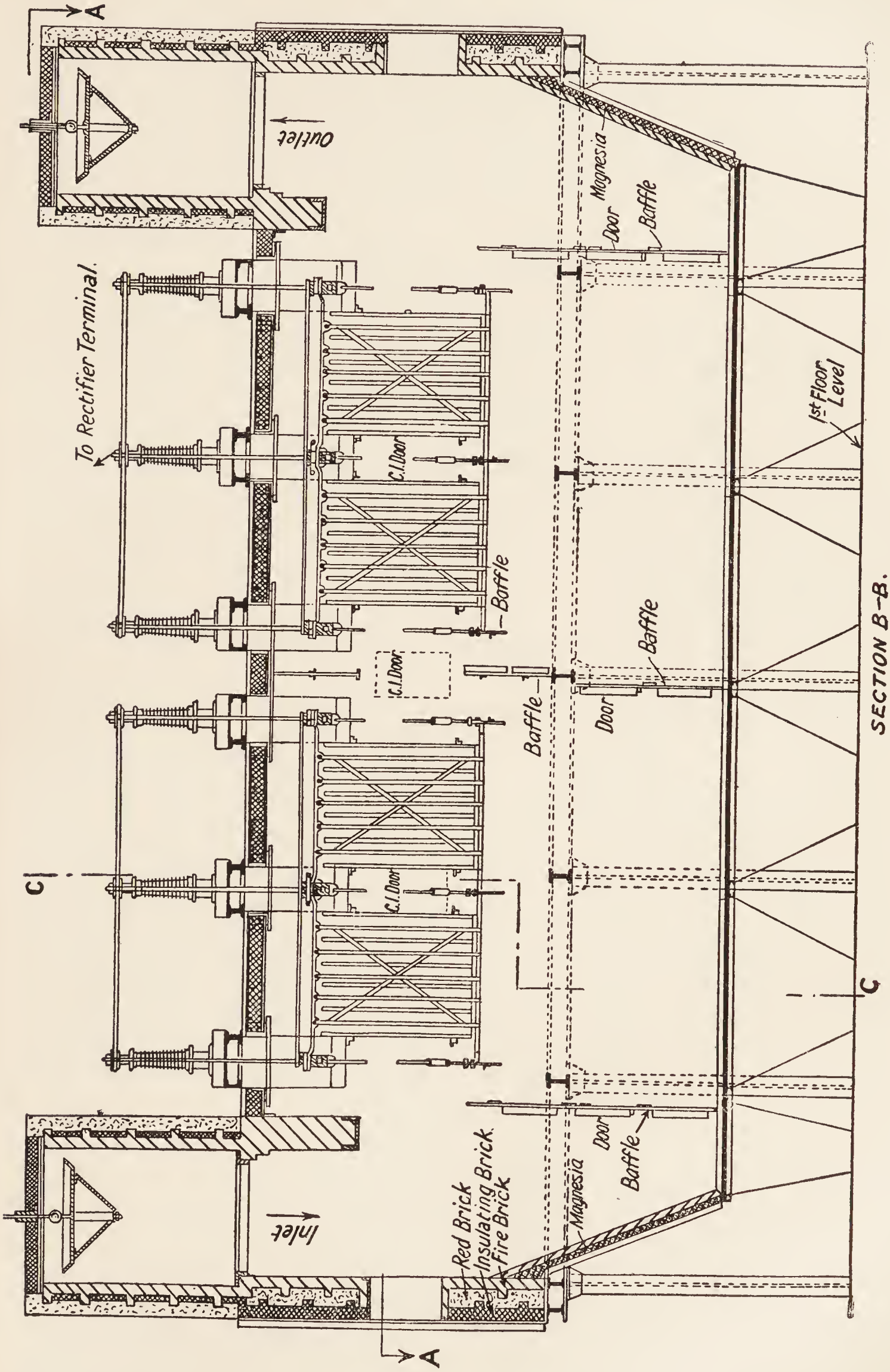


Fig. 18.

The application of electrostatic precipitation to the cleaning of roaster gases from mechanical pyrites furnaces is a field that has been somewhat neglected both in America and in this country. In the United States isolated installations were put in as far back as 1916, but it was

not until the co-operation of one of the largest acid producers was secured that results were obtained justifying the faith of the adherents of electrical precipitation. For some time past a precipitator has been in operation cleaning the gases from mechanical furnaces burning roughly 70 tons of pyrites per 24 hours, with an average efficiency of over 98 p.c. About 6 tons of dust are recovered per week, a large part of which would ordinarily have gone forward to block the washing towers, coolers, filters, &c. The temperature of the gases is over 500°C.; the power consumption of the cleaning plant is only 3 kw. per hour.

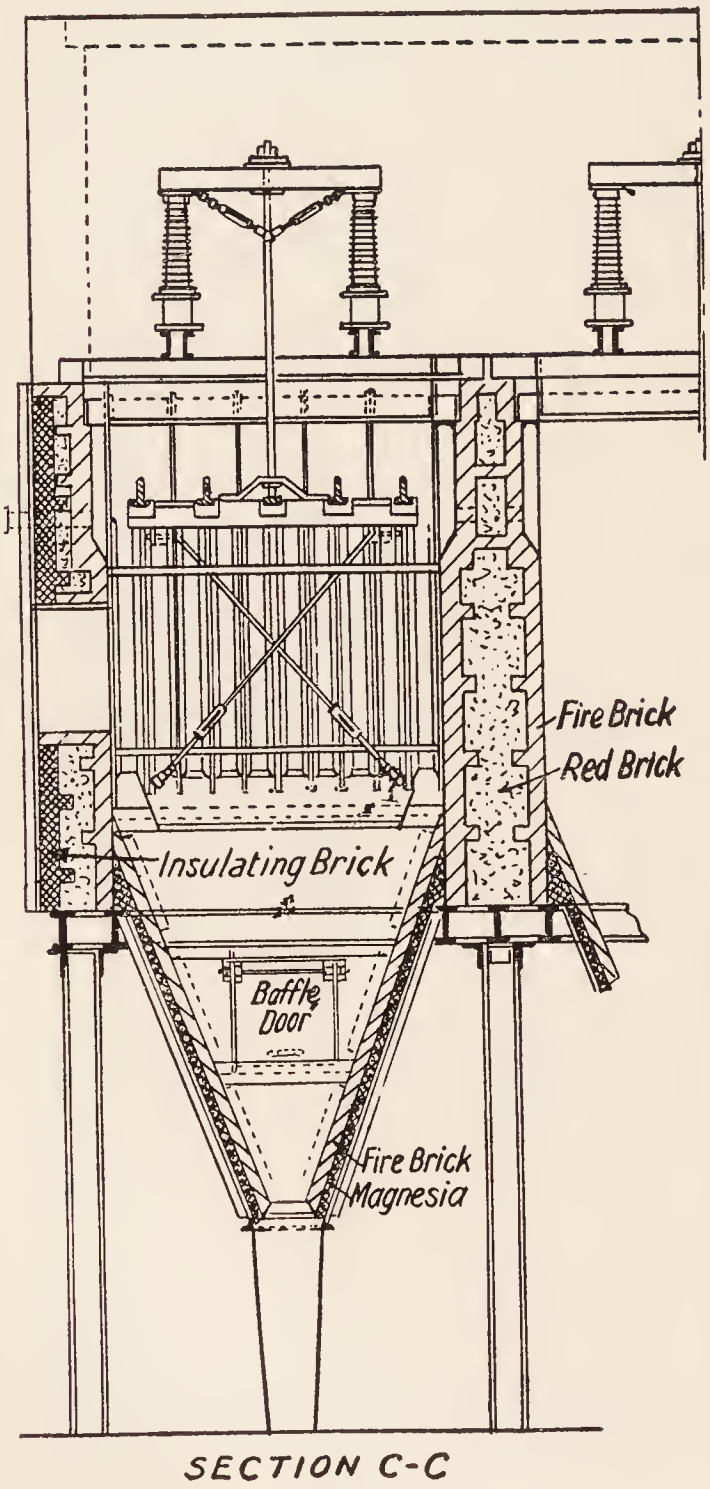


FIG. 19.

Fig. 18 shows a longitudinal section through one chamber, Fig. 19 a cross-section, and Fig. 20 a plan. The discharge members are angle-iron frames suspended from heavy cast-iron bearers hung from suspension rods, which pass through the top of the chamber through specially constructed leading-in insulators, and are bolted to transverse channels resting on petticoat insulators.

By virtue of these suspension rods and roller bearings, which take the weight of the cast-iron bearers, the whole electrode system is free to expand and contract according to changes of temperature.

The receiving electrodes are reinforced M.S. plates suspended parallel to the flow of the gases. Holes are provided in the sides of the steel casement through which rods can be intro-

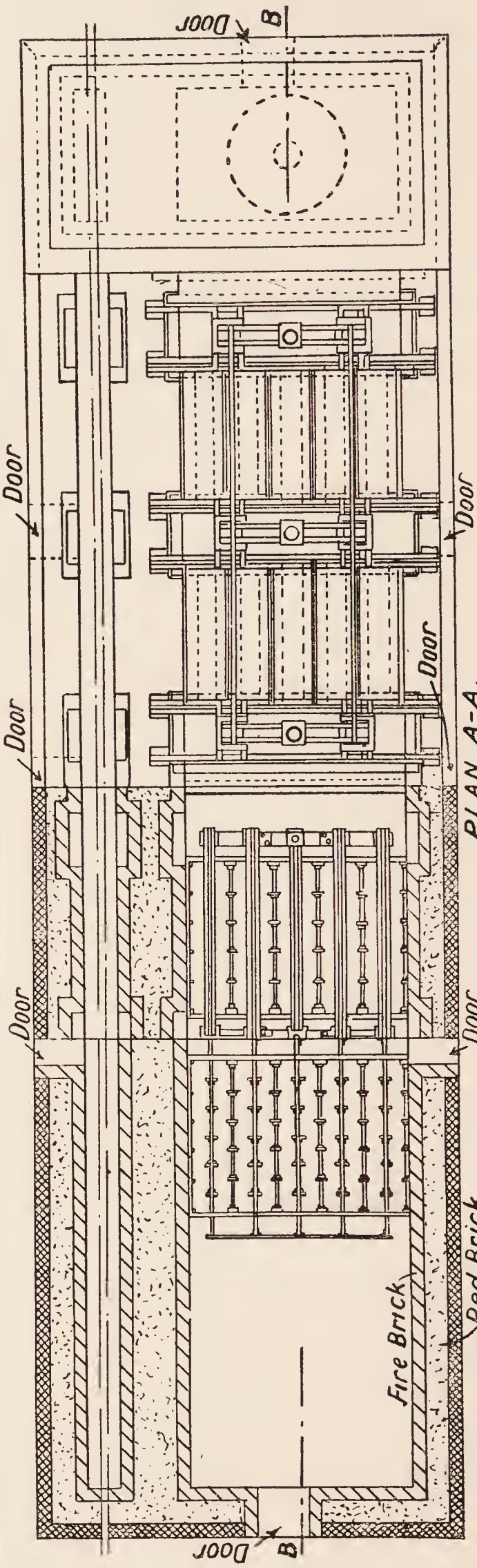


FIG. 20.

duced for jarring both the discharge and the receiving electrodes. It is found that most ores roasted for acid making do not cling very tightly to the electrodes and fall off without

rapping. Others are inclined to stick and make the provision of rapping gear desirable.

The precipitating chambers are provided with the usual inlet and outlet cone valves operated by means of hand winches, which allow any one unit to be readily isolated for purposes of inspection or cleaning out. The top of the chambers is fitted with removable inspection covers to make the electrodes easily accessible. The bottom may be constructed as one long hopper with a conveyor for discharging the accumulated dust, or a number of smaller hoppers may be provided with slides and telescopic pipes for conveying the dust straight into hooded trucks.

In Germany a type of electrical precipitator for cleaning pyrites roaster gases in oleum plants was evolved during the war, comparing very favourably with one seen in Fig. 18.

It is on the plate-and-wire principle, of simple and light design yet of ample strength. The problem of insulating the high-tension discharge members has been solved in a very felicitous manner, the supporting insulating framework being suspended from bearers resting on the side walls. Suitable hand-operated hammers are provided for rapping both the discharge and receiving electrodes; this is done about once every 3 hours.

The chambers are always built in twin sets, and are so dimensioned that while one chamber is off the whole of the gas can be handled by the other at a slightly reduced efficiency. The general lay-out of the chambers and the connecting inlet and outlet flues is very similar to the design described above.

The walls are of brickwork well secured by buckstaves and tie-rods, steel casements being dispensed with. German practice favours the laying of the high-tension conductor from the rectifier house to the precipitating chambers in covered troughs below floor level, where it is free from fume and dust and out of reach of the workmen engaged about the plant. At a point close to the chamber the conductor emerges inside a vertical pipe and enters a junction box, where connection is made to the high-tension busbars inside the chamber. Each chamber has its separate lead branching off through an automatic circuit breaker from a point in the circuit of the common generating set. These breakers are fitted with secondary contacts, which when the breaker comes out close an auxiliary circuit connected to a signal light and hooter.

Thus, should a short-circuit occur in one chamber the furnaceman is at once advised and can see by a glance at the signal light which chamber is off. Without having to touch the electrical machines he puts the breaker in again. If it stays in the disturbance was only a passing one; if it will not stay in the cause of the trouble can in most cases be located by closing the cone valves of the compartment in question and opening an inspection cover. As a matter of fact, these installations work very smoothly indeed and require very little attention.

There is no attendant attached to them beyond the man in charge of the roasting furnaces.

The charges for repairs and maintenance are found to be very small, no warping of the steelwork has been noticed, and there is no corrosion, as the working temperature in the precipitator is always above 350°C.

The power consumption for an installation capable of cleaning the gases from roasting 15 tons of 48 p.c. pyrites per 24 hours is about 3 kw. per hour.

The following figures were taken on different days at a plant cleaning the gases from a Wedge furnace roasting 18 tons per 24 hours of Westphalian Meggen pyrites:—

Temperature at precipitator inlet °C.	Grams of dust per cub. m.		Efficiency p.c.
	Dirty gas	Clean gas	
349	2·299	0·030	98·7
370	3·016	0·003	99·8
382	3·091	0·059	98·3
315	2·306	0·024	98·9

Over 20 such precipitators have been erected on the Continent since 1914, chiefly in Germany.

In France also a number of leading sulphuric acid manufacturers have adopted electrical precipitation for cleaning the sulphur dioxide gases from mechanical roasters, the type favoured being vertical C.I. pipes with alloy steel wires suspended therein as discharge members.

The pipes are encased in brickwork or reinforced concrete chambers with division walls to form inlet and outlet connecting flues, in which cone dampers are fitted.

The space below the pipes is hopper-shaped and has a screw conveyor with luted discharge for removing the precipitated dust.

These installations are reported to be working successfully and to show efficiencies of 96 p.c. and over.

The installation of electrical precipitators is conducive to raising the general efficiency of a sulphuric acid works burning pyrites smalls in mechanical furnaces, in that it eliminates laborious flue cleaning, washing down of Glover and Gay-Lussac towers, cleaning out of sludge from coolers, tanks, and pumping machinery, with the attendant loss of acid, nitre, and production. In addition, it ensures the production of a perfectly clean Glover acid, which, apart from the possible presence of arsenic, will stand comparison with the product obtained from burning brimstone. Owing to the high temperature at which the precipitation of the dust takes place, the arsenic contents of the acid produced is not materially affected, it being understood that no substance present as a true vapour can be electrically precipitated, unless some other body be added to the gas which will form a liquid or solid compound with the vapour.

If arsenic is to be removed by electrical precipitation as well as the mineral dust, the gas must be cooled below the condensation point of arsenic trioxide, preferably after the dust has been eliminated at a prior stage. Such an installation has been working for some time, consisting of a dust precipitator of the type referred to above, followed by a cooling tower and lead-pipe type of precipitator, in which the condensed arsenious oxide and sulphuric acid are brought down. The purity of the issuing gas has been tested by optical means and by the Marsh test with negative results in both cases.

The following are some interesting figures obtained with:—

(1) A mechanical dust-catcher, and

(2) An electrical dust precipitator,

followed in both cases by an electrical de-arsenicator.

The gases emerging from the dust-catcher at 400°C. are cooled in towers to 30°C. before de-arsenication.

Daily charge of pyrites=15 tons containing 48 p.c. sulphur.

Acid delivered from cooling towers=5·6 cubic metres an hour; sp.gr. 1·32; containing 4·65 grams of arsenic per litre.

There were recovered daily in the electrical de-arsenicator from :—

(1) 28 kilos. of sludge containing 80 p.c. of lead and 0·5 p.c. arsenic.

(2) 850 grams. of sludge containing 42·7 p.c. of lead and 0·32 p.c. of arsenic.

The very much lower efficiency of the mechanical dust-catcher is shown up very strikingly by these figures.

In the United States of America there are numerous installations of electrical precipitators at work, treating all manner of gases and materials suspended therein. Owing to the peculiar conditions prevailing there, both the volumes of gas treated per unit of time and the amount of material recovered greatly exceed anything accomplished in this country.

At the Anaconda Copper Company an installation has been built to handle no less than 3 million cubic feet per minute, from which it is estimated to recover 240 tons of metalliferous dust in 24 hours.

The United Verde Copper Company has a total of 3600 precipitation pipes supplied with high-tension current from twelve 25 k.v.a. motor generators, to recover the values carried away by the waste of gases from its roasting furnaces, blast furnaces, and convertors.

The research Corporation of New York have invaded quite new fields by some of their later installations which were erected, not for the purpose of reducing dust losses on smelting operations, but solely for cleaning air. For several years during the war the air from workrooms at an American small-arms factory, where carding, buffing, and grinding wheels were operating, was cleaned by electrical precipitation. A volume of 50,000 cub. ft. of air at 70°F. was treated per minute, and several cartloads of dust per week were removed from it. Incidentally, researches made during the war have shown that after passing air through an electrical precipitator, it is not only free from dust particles, but sterilised as well. This may probably be attributed to the removal of the solid particles which carry bacteria, and to the toxic effect of the ozone and oxides of nitrogen produced by the corona discharge.

At the Stace Mining Company electrical precipitation was resorted to after cyclones, bag filters, and scrubbers had been tried without success. The problem was to remove the fine slate dust arising from the crushing plant, where slate rock was passed through rollers for the preparation of slate dust for roofing material. Over 100,000 cub. ft. of air are cleaned per minute, and several tons of material are recovered per week.

An interesting installation is under construction for cleaning the air from a works where large numbers of piston rings for gas engines are cut and ground. The precipitator will replace a bag filter, which was found unsuitable owing to the cloth cutting, the difficulty of keeping the bags clean, and the excessive power consumption required. A flue type of precipitator will be installed, having a cross-section of 14 by 10 feet, and a capacity of 25,000 cub. feet of air per minute. In another case the air from tumbling barrels in an iron foundry, carrying sand and iron dust in suspension, is to be cleaned electrically, a cyclone installation having proved incapable of retaining the fine dust.

Installations of considerable magnitude are being installed by the Braden Copper Company of Chile and the Cerro de Pasco smelter of Peru for recovering metalliferous flue dust.

Altogether there are now over 180 electrostatic recovery plants operating in different parts of the world. H. J. B.

PREHENITENE *v.* CYMENES.

PREHENITOL *v.* PHENOL AND ITS HOMOLOGUES.

PREHNITE. Acid calcium aluminium silicate $H_2Ca_2Al_2(SiO_4)_3$, crystallised in the orthorhombic system. Distinct crystals are rare, the mineral usually forming globular or botryoidal groups with a crystalline surface. The colour is a characteristic green or yellowish-green of various shades. Sp.gr. 2·80–2·95, H=6. It is a mineral of secondary origin and of common occurrence in association with zeolites, in the steam-cavities of basic igneous rocks, though it also occurs in veins in granite and gneiss. It is therefore sometimes classed with the zeolites (*q.v.*), but its small amount of water (4·4 p.c.) is expelled only at a red heat. The best crystals come from Bourg d'Oisans in Isère, and handsome specimens are abundant in the Paterson district in New Jersey, and the neighbourhood of Glasgow and Edinburgh. Large masses have been found at Cradock, in Cape Colony. Prehnite has occasionally been used as a gem-stone. Small faceted stones have been cut from clear crystals, and the cloudy crystalline aggregates are sometimes effective when polished with a carved surface.

L. J. S.

PRICEITE *v.* COLEMANITE.

PRICKLY COMFREY, *Symphytum asperrimum* (Donn). A succulent perennial plant which has been highly praised as a green fodder for farm animals. It is usually grown from root cuttings, and yields many crops per year. It should be cut before flowering and then has the composition (Kellner)—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
88·5	2·5	0·3	5·0	1·7	2·0

Only about 0·9 p.c. of digestible proteid is present. It can be made into hay if cut while young. Kellner gives as the average composition of such hay—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
15·0	20·7	2·7	35·1	11·5	15·0

The protein includes 9·5 p.c. of digestible proteid. H. I.

PRICKLY PEAR, *Opuntia Tuna* (Mill.). A native cactus of the West Indies and Mexico, now introduced and become naturalised in many hot countries, in some of which, *e.g.* Cape

Colony, New South Wales, St. Helena, it has become a troublesome weed. The fruit is sometimes eaten: according to König, it consists of—

Rind	Flesh	Seeds
36·5	60·2	3·3

and the flesh contains—

Water	Protein	Sugar	Sugar-yielding carbohydrates	Fat	Ash
91·5	0·7	5·3	1·4	trace	0·3

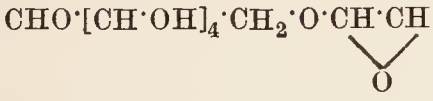
Both the fruit and the 'leaves' are covered with sharp spines, which have to be removed before the fruit can be eaten. The succulent leaf-like branches, after the spines are removed by burning, can be used as food for animals in dry seasons, when green food is scarce. A specimen of these branches, grown in the Transvaal, was examined by the writer and found to contain (J. Agric. Science, 1908, 3, 29)—

Water	Protein	Ether extract	N-free extract	Crude fibre	Ash
93·8	0·4	0·1	3·9	0·6	1·1

The ash was rich in potash and lime.

H. I.

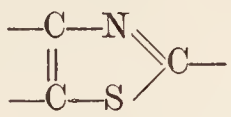
PRIMEVEROSE. A sugar obtained from two glucosides, *primeverin* and *primulaverin*, found in *Primula officinalis* (Jacq.). Anhydrous crystals, m.p. 209°–210°. It shows mutarotation, initially $[\alpha]_D$ +22·70°, finally $[\gamma]_D$ −3·43°. Reduces Barreswil's solution, gives an osazone, m.p. 224°–225°, and on hydrolysis gives one mol. of dextrose and one mol. of xylose. Constitution:



(Goris and Vischniac, Compt. rend. 1919, 169, 871, and 975).

PRIMROSE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PRIMULINE AND ITS DERIVATIVES (Syn. **Thiazol dyestuffs** or **Thiobenzenyl dyestuffs**). Under this heading will be considered the colouring matters characterised by the presence of the chromophoric grouping



which are derived from the condensation-products obtained by the action of sulphur upon paratoluidine and metaxylidine.

History.—The preparation by Dahl and Co. (Eng. Pat. 14232, 1885) of a supposed thio-*p*-toluidine isomeric with the diaminoditolylsulphide of Merz and Weith led the writer in 1887 to study the action of sulphur upon *p*-toluidine. It was then found that if these substances were caused to react at the boiling-point in the proportion of 2 mols. of the latter to 4 atoms of the former, the loss of hydrogen sulphide which occurs corresponds with the equation:

$$2C_7H_7\cdot NH_2+S_4=C_{14}H_{12}N_2S+3H_2S$$

The product obtained, which is now known as *dehydrothiotoluidine*, was a crystalline base forming long yellow needles of m.p. 191°, and b.p. 434°. It was insoluble in water, more readily soluble in alcohol, and formed sparingly soluble yellow salts. On treatment with fuming sulphuric acid it gave rise to a very sparingly soluble mono-sulphonic acid, characterised by forming a colourless sparingly soluble ammonium salt. Although the dehydrothiotoluidine contained only one diazotisable amino group, it was found that its diazo compound and also the diazo derivative of its sulphonic acid, when coupled with suitable amines and phenols (or sulphonic acids thereof) gave a series of colouring-matters which all dyed cotton directly without a mordant, this being the first known case of mono-azo dyestuffs having this property. Furthermore there was obtained, by the action of ammonia upon the diazotised dehydrothiotoluidine sulphonic acid, a bright greenish-yellow dyestuff also possessing a substantive affinity for cotton.

A further study of the action of sulphur upon *p*-toluidine revealed the fact that in addition to dehydrothiotoluidine there were also produced higher condensation-products of the latter, these compounds being formed according to the equations:—

$$3C_7H_7\cdot NH_2+S_8=C_{21}H_{15}S_2N_3+6H_2S$$
and $$4C_7H_7\cdot NH_2+S_{12}=C_{28}H_{19}S_3N_4+9H_2S$$

These more condensed bases ('primuline bases') were obtained in larger amount by increasing the proportion of sulphur to 4½–5 atoms to 1 mol. amine. Although possessing in general properties similar to dehydrothiotoluidine, they are of a deeper yellow colour, more insoluble, and melt and boil at higher temperatures. Like dehydrothiotoluidine they contain a single diazotisable amino group and their diazo compounds upon combination with amine- and phenolsulphonic acids were found to produce azo- dyestuffs very similar to those derived from dehydrothiotoluidine and likewise possessing a direct affinity for cotton. In seeking for the cause of this affinity the discovery was made that the soluble alkaline salts of the mono-sulphonic acids of the above higher condensation products themselves dyed cotton directly, imparting thereto a primrose-yellow colour. Furthermore, it was found that by immersing the cotton thus dyed in a weak solution of nitrous acid the amino group of the compound could be readily diazotised without disturbing the affinity of the compound for the fibre, and upon then bringing the cotton into a solution of an appropriate amine or phenol, a series of new dyestuffs were produced varying, according to the component used, from reddish-yellow to red, violet, and blue. These azo compounds being built up within the fibre substance, were fixed upon the cotton with a firmness far superior to that of the shades dyed with ordinary 'direct' or 'salt' colouring-matters, and possessed in consequence a high degree of fastness to washing, soap and alkalis.

Under the name of 'Primuline' the sodium salt of the above-described sulphonic acid of the higher thionated *p*-toluidine was first manufactured and introduced into commerce by Messrs. Brooke, Simpson and Spiller, of London, in 1887, and employed for the production of so-called 'Ingrain Colours' by the above process of diazotising and developing upon the fibre (A. G. Green, The Dyer, 1887, 7, 101; J. Soc.

Chem. Ind. 1888, 7, 179; Chem. Soc. Trans. 1889, 55, 227). By reason of the fastness of the shades produced, more especially of the red obtained with β-naphthol, primuline at once acquired a high technical importance and was manufactured by various firms under the names of 'Polychromine,' 'Thiochromogen,' 'Sulphine,' 'Aureoline,' &c., all of which names have, however, now become obsolete.

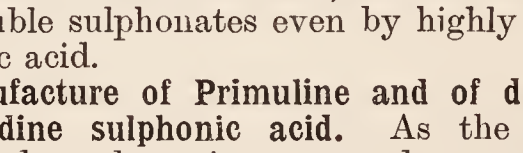
The important principle of producing fast colours upon the fibre by dyeing with a substantive colouring-matter containing an amino group and afterwards diazotising and developing ('ingrain process') has since been extended to a large number of other dyestuffs (Diaminogen, Diazo Blacks, Diamine Blacks and Blues, &c.), especially for dyeing fast navy blues and blacks.

In addition to the colours produced upon the fibre from primuline by diazotisation and development, it was also found that a reddish-yellow of extreme fastness to light and washing was obtainable by oxidation of the dyed cotton with a solution of sodium or calcium hypochlorite. The application of the latter reaction to Primuline in substance, and to the sodium salt of dehydrothiotoluidine sulphonic acid, gave rise to valuable direct yellow dyestuffs fast to light ('Chloramine Yellow,' 'Oxyphenine,' 'Chlorophenine Yellow,' &c.). It was also found by Green and Evershed that the diazoamino compounds derived from Primuline or from dehydrothiotoluidine sulphonic acid or both, were substantive cotton dyestuffs possessing a bright greenish-yellow shade ('Thiazol Yellow,' 'Clayton Yellow,' 'Turmerine'). These were first brought upon the market by the Clayton Aniline Co. and by Bayer & Co.

The trimethylammonium chloride of dehydrothiotoluidine, obtained by heating the base with methyl alcohol and hydrochloric acid was found by Green and Lawson (Ber. 1889, 22, 971) and by Rosenheck to be a valuable greenish-yellow basic dyestuff ('Thioflavine T'). Methylated derivatives of primuline were also introduced by Cassella & Co. as direct yellow dyestuffs for cotton under the name of 'Thioflavine S,' whilst the condensation product of primuline with formaldehyde was sold by Brooke, Simpson and Spiller for the same purpose.

The dehydrothioxylidine obtained by Schultz and Anschütz by heating *m*-xylidine with sulphur (Ber. 1889, 22, 582) was employed by the Berlin Aniline Co. for the preparation of a valuable pink cotton dyestuff ('Erica') by combination of its diazo compound with the α-naphthol-ϵ-disulphonic acid.

The constitution of dehydrothiotoluidine was investigated by P. Jacobsen (Ber. 1889, 22, 330); Gattermann (*ibid.* 1889, 22, 422); Anchütz and G. Schultz (*ibid.* 1889, 22, 580); A. G. Green (*ibid.* 1889, 22, 968; Chem. Soc. Trans. 1889, 55, 227); and Pfitzinger and Gattermann (Ber. 1889, 22, 1063). The last-named authors finally established its constitution as that of a *p*-aminobenzenyl-aminothiocresol (syn. *p*-aminophenyl-toluthiazol):



By deamination it was found to give rise to a benzenylaminothiocresol identical with that obtainable by oxidation of an alkaline solution of thiobenzoyl-*p*-toluidine

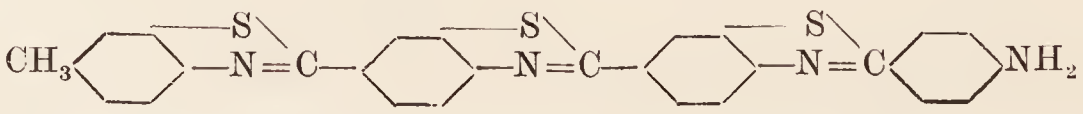
$$C_6H_5\cdot CS\cdot NH\cdot C_6H_4\cdot CH_3$$

It thus appears probable that in the action of sulphur upon *p*-toluidine the methyl group of the latter is first attacked with production of *p*-amino-dithiobenzoic acid $NH_2\cdot C_6H_4\cdot CS\cdot SH$, which reacts at once with the second molecule of *p*-toluidine giving the *p*-amino-thiobenzoyl-*p*-toluidine $NH_2\cdot C_6H_4\cdot CS\cdot NH\cdot C_6H_4\cdot CH_3$. The latter is then converted into dehydrothiotoluidine by the withdrawal of 2 atoms of hydrogen as hydrogen sulphide.

Assuming that the further action of sulphur proceeds in a similar manner, the higher thionated bases will have the constitution:



and



Experiments conducted by the writer (unpublished) support the conclusion that commercial Primuline consists almost entirely of the mono-sulphonate of the first of these compounds. The latter also may sometimes be present to a small extent (as sulphonate), and is produced as chief product by heating dehydrothiotoluidine (2 mols.) with sulphur (4 atoms) (Green, Ber. 1889, 22, 970; Kalle & Co., D. R. P. 61204). In regard to the properties of these two bases it may be mentioned that the first melts at about 220°, is insoluble in alcohol, but soluble in nitrobenzene. The second melts at about 340°, and is insoluble in nitrobenzene, whilst its sulphonic acid has a more intense yellow colour than the sulphonic acid of the first.

Even with production of the tetranuclear base, the condensation by sulphur does not come to a stop, for upon heating *p*-toluidine with still more sulphur (3 atomic proportions to 1 mol. amine) products of extremely high melting-point are formed, which are solid at 300°, insoluble in all solvents, and not converted into soluble sulphonates even by highly fuming sulphuric acid.

Manufacture of Primuline and of dehydrothiotoluidine sulphonic acid. As the above-mentioned condensations proceed concurrently, it is not possible to obtain single products, but mixtures in different proportions of dehydrothiotoluidine with its higher thionated derivatives are always produced. Thus by reacting upon 2 mols. of *p*-toluidine with the following

proportions of sulphur, the products consist of :—

With 4 atoms of sulphur	10 p.c. unaltered *p*-toluidine 50 p.c. dehydrothiotoluidine 40 p.c. primuline base
With 4½ atoms of sulphur	4 p.c. unaltered *p*-toluidine 33 p.c. dehydrothiotoluidine 63 p.c. primuline base
With 5 atoms of sulphur	2 p.c. unaltered *p*-toluidine 23 p.c. dehydrothiotoluidine 75 p.c. primuline base

The best proportions with respect to the quality of the Primuline obtained is that of 4½ atoms of sulphur to 2 mols. of *p*-toluidine. For the preparation of dehydrothiotoluidine base it is best to employ 2 atoms of sulphur to 2 mols. of *p*-toluidine and to subject the melt to a fractional distillation *in vacuô*. The excess of *p*-toluidine and a little diaminoditolyl sulphide pass over first and are then followed by pure dehydrothiotoluidine which crystallises on cooling.

The Primuline Melt is made in an enamelled iron pot of about 200 gals. capacity which is set in brickwork and provided with an enamelled iron agitator (*see* Fig. 1). The lid of the pot also carries a thermometer tube, and a hole for charging and emptying which is closed by a flange. Connected with the lid is a cast-iron pipe (preferably enamelled) of 8–10 ins. internal diameter and about 40–50 ft. long. This pipe

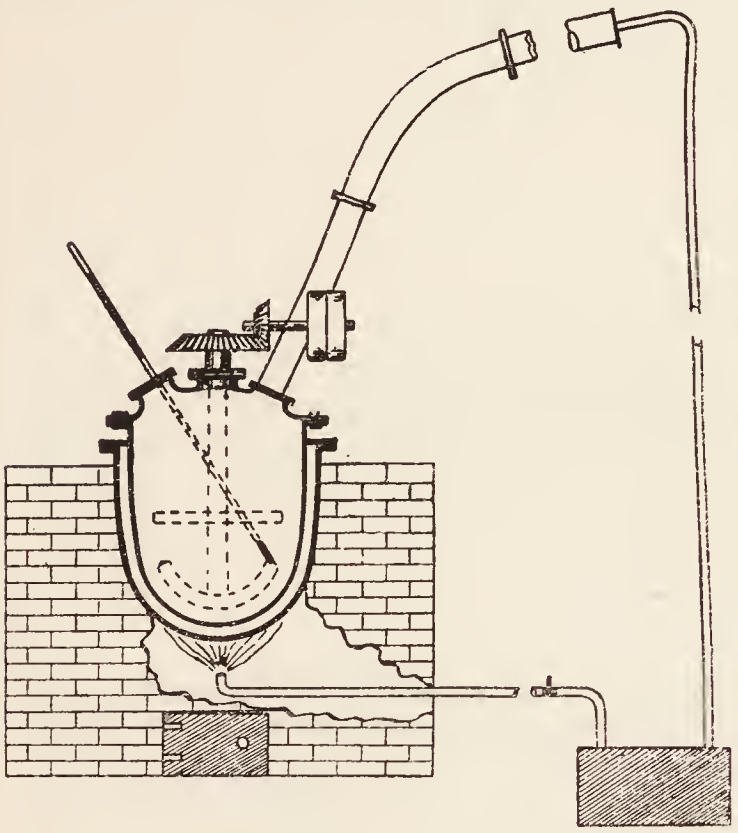


FIG. 1.

is inclined upwards at an angle and serves as an air cooler to condense and return to the pot the *p*-toluidine which is carried off as vapour by the current of hydrogen sulphide. The whole or a part of the pipe can if necessary be cooled by a spray of water. From the further end a smaller pipe (2 ins. diam.) carries the gas, which should then be quite cold, to an iron box, in which a little *p*-toluidine collects, and thence it passes to the furnace where it is burnt under the pot, which it serves to heat.

The pot is charged with 1000 lbs. of *p*-toluidine and 670 lbs. of sulphur. This is heated to the boiling-point for several hours, the temperature slowly rising as the reaction proceeds. The evolution of hydrogen sulphide commences at 170° and is completed when the temperature reaches 270°. The agitator is then stopped and the hot fluid is transferred from the pot under air pressure by means of a pipe inserted through the charging hole. After cooling and solidifying, the product is reduced to powder by means of a disintegrator. The yield is about 1125 lbs.

The Sulphonation is performed in an enamelled iron jacketed pan of 220 gals. capacity provided with cooling pipes through which cold water can be circulated (*see* Fig. 2). The contents of the pan can be rapidly stirred

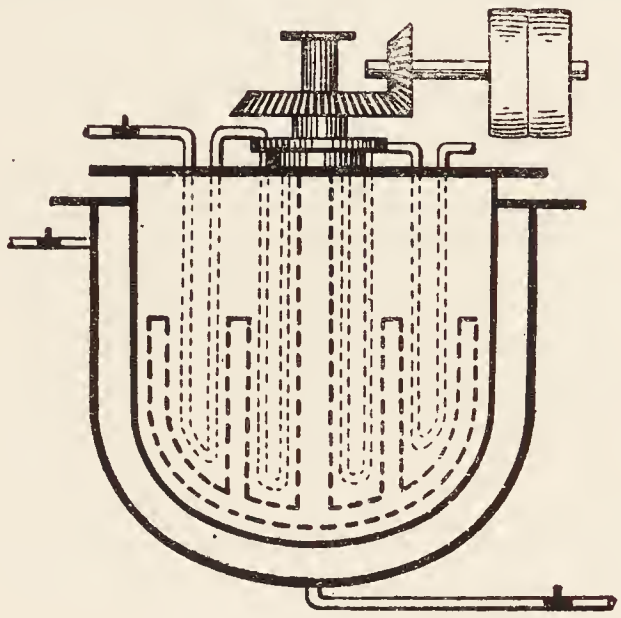


FIG. 2.

by means of an agitator, the blades of which pass between the loops of the cooling pipes.

The ground melt (400 lbs.) is dissolved under rapid agitation in 1000 lbs. of 100 p.c. sulphuric acid (final temperature about 90°). There is then added slowly, while the mixture is kept rapidly agitated and well cooled, 800–900 lbs. of fuming sulphuric acid, 70 p.c. SO_3. The temperature is not allowed to rise above 40°, and the operation lasts about 6 hours. The sulphonation is complete when a small sample precipitated in water dissolves to a perfectly clear solution in boiling dilute ammonia. The mixture is then blown out of the pot by compressed air through the hollow spindle of the agitator and is run by means of a lead pipe into a wooden vat containing about 3000 gals. of cold water in which the dehydrothiotoluidine and primuline-sulphonic acids are thrown down as a voluminous orange-yellow precipitate. This is filtered off through a wooden filter-press in which it is thoroughly washed with water until all mineral acid is removed (*see* Fig. 3). In order to effect the separation of the dehydrothiotoluidine sulphonic acid from the primuline sulphonic acid, the sparing solubility of the ammonium salt of the former is made use of. The mixed sulphonic acids, in the form of the wet press cake, are stirred up with cold concentrated ammonia in a wrought-iron vessel provided with an agitator. The primuline dissolves whilst the ammonium dehydrothiotoluidine sulphonate separates out as a silky crystalline precipitate. The mixture is transferred to a suction filter and the precipitate washed with a little water until nearly white. Upon adding

common salt to the filtrate, the primuline is thrown down as a dark yellow granular precipitate, which after drying is ground with sufficient common salt to bring it to standard strength. A small quantity which remains in the filtrate is recovered by adding the latter to the acid precipitating vat. The yield under the best conditions amounts to 530–560 lbs. of ammonium dehydrothiotoluidine sulphonate, and 1700–1800 lbs. of standard primuline, from 1000 lbs. of *p*-toluidine.

Application of Primuline ('ingrain process'). Primuline is chiefly employed in cotton dyeing, especially for dyeing fast reds upon cotton warps. It is also used to a smaller extent for dyeing silk. Owing to the want of fastness in the yellow condition, it is little used as a direct colouring-matter, but is employed almost exclusively for the production of various ingrain-colours by diazotisation and development on the fibre, the most important of these colours being the red obtained by combination with β-naphthol. The shades thus produced possess a high degree of fastness to soaping, milling, and acids, although not especially resistant to light. The following shades are obtained by

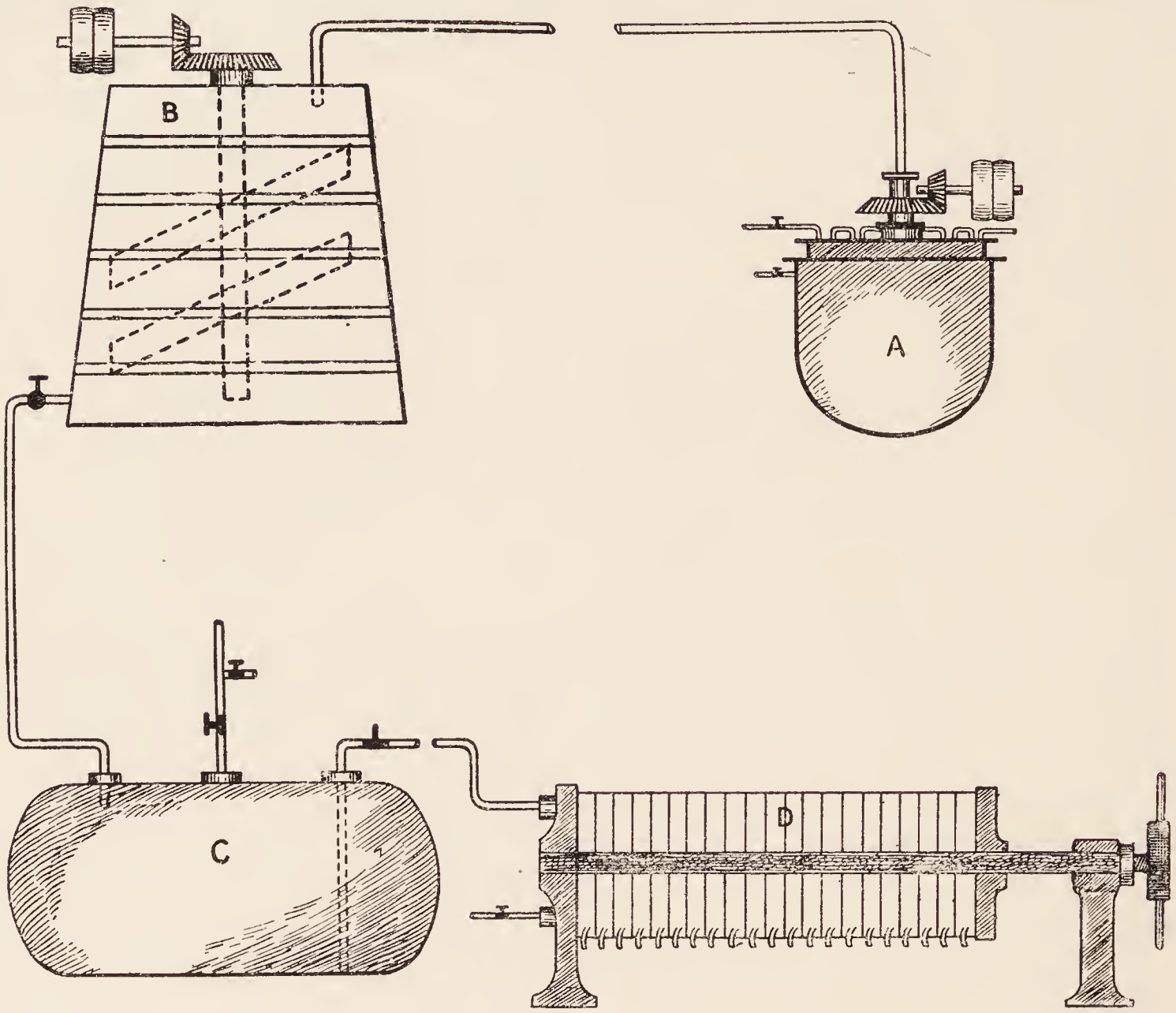


FIG. 3.

development with the respective phenols and amines :—

Phenol $C_6H_5 \cdot OH$	Yellow
Phenylmethylpyrazolone $C_3H_2N_2O(C_6H_5)(CH_3)$	Yellow
Resorcinol $C_6H_4(OH)_2$	Orange
2 : 3Dihydroxyquinoline $C_9H_5N(OH)_2$	Orange
m-Phenylenediamine $C_6H_4(NH_2)_2$	Reddish-brown
m-Tolylenediamine $C_6H_3(CH_3)(NH_2)_2$	Reddish-brown
α-Naphthol $C_{10}H_7 \cdot OH$	Maroon
β-Naphthol $C_{10}H_7 \cdot OH$	Red
α-Naphthol-*p*-sulphonic acid $C_{10}H_6(OH)(SO_3Na)(1:4)$	Crimson
β-Naphthol-di-sulphonic acid R $C_{10}H_5(OH)(SO_3Na)_2(2:3:8)$	Maroon
α-Naphthylamine $C_{10}H_7 \cdot NH_2$	Purple
Hydroxy-α-naphthylamine methyl ether $C_{10}H_6(OCH_3)NH_2$	Reddish-blue
2 : 3-Hydroxynaphthoic-anilide $C_{10}H_6(OH)CO \cdot NHC_6H_5$	Bordeaux
p-Amino-di-phenylamine $C_6H_5 \cdot HN \cdot C_6H_4 \cdot NH_2$	Olive-green

The reactions take place on the fibre with great ease and rapidity and follow the general equations for the formation of azo- dyestuffs :—

(*a*) $\underset{\text{(primuline)}}{P \cdot NH_2} + NO(OH) = \underset{\text{(diazo primuline)}}{P \cdot N_2 \cdot OH} + H_2O$

(*b*) $\underset{\text{(diazo-prim.)}}{P \cdot N_2 \cdot OH} + \underset{\text{(phenol or amine)}}{HX(OH \text{ or } NH_2)} =$

$$P \cdot N_2 \cdot \underset{\text{(ingrain colour)}}{X(OH \text{ or } NH_2)} + H_2O$$

[In these equations, P stands for the radicle of Primuline $C_{21}H_{12}S_2(SO_3H)'$.]

The dyeing process is carried out as follows : The cotton is dyed from a boiling bath containing from 2–5 p.c. of the dyestuff together with an amount of common salt depending on the volume of the bath. It is then well rinsed in cold water to remove loose colour and steeped for one minute in a cold bath containing sodium nitrite (2½ p.c. on the weight of the cotton) and hydrochloric acid (7½ p.c.). The cotton is then

again rinsed in water and brought into a cold bath containing the phenol or amine to be employed as developer, *e.g.* a solution obtained by dissolving one part of β-naphthol and one part of caustic soda in 400 parts of water. Phenols are employed in alkaline solution, amines in slightly acid solution.

In the dyeing of cotton warps the process is rendered very simple by employing a series of baths in line, through which the cotton passes continuously. The first bath contains a boiling solution of primuline, the second cold water for rinsing, the third a cold solution of nitrite and acid, and the fourth again cold water, the fifth is the developing bath, and the last a final washing bath. The time of passage of the cotton through the entire series of baths is only from 3 to 5 minutes and the warp leaves fully dyed.

A fast orange-yellow, possessing a high degree of fastness to light, washing and other agents, is obtained by treating cotton dyed with primuline with a solution of calcium hypochlorite of about ¾°Tw. The reaction which occurs is probably as follows:

$$2P{\cdot}NH_2+O_2=P{\cdot}N:N{\cdot}P+2H_2O$$

All the ingrain colours can be readily reduced to the original yellow primuline by boiling the dyed cotton for a few minutes in a solution of sodium hydrosulphite. The regenerated colour can then be rediazotised and again developed as desired.

In the diazotisation of primuline, care must be taken that the material is not exposed to strong light, as the diazo compound, although stable in the dark, is decomposed rapidly by sunshine according to the equation:

$$P{\cdot}N_2{\cdot}OH=P{\cdot}OH+N_2$$

Nitrogen is evolved and the corresponding phenol is produced. This latter is of a pale yellow shade and no longer has the property of combining with phenols or amines to form azo colours. Upon this property has been based a process for producing coloured designs and photographic patterns upon textile fabrics, which is known as the 'diazotype process' (A. G. Green, C. F. Cross and E. J. Bevan, J. Soc. Chem. Ind. 1890, 9, 1001; Ber. 1890, 23, 3131; Eng. Pat. 7453, 1890). In this process, the material (cotton, silk, or paper) which has been dyed with primuline and diazotised, is exposed to light under the design or object which it is desired to copy, until the unshaded portion is no longer capable of combining with phenols. The material is then dipped or brushed with the developing solution when the pattern appears in the respective colour upon a pale yellow ground (*v.* PHOTOGRAPHY).

Clayton Yellow (Syn. Thiazol Yellow, Turmerine, Mimosa). These dyestuffs are mixtures of the diazoamino compounds, $D{\cdot}N_2NH{\cdot}D$, $D{\cdot}N_2{\cdot}NHP$, and $P{\cdot}N_2{\cdot}NH{\cdot}P$ (in which D and P respectively represent the radicles of dehydrothiotoluidine sulphonic acid and of primuline sulphonic acid).

They are prepared by the action of ammonia upon the diazo compounds of the above amine-sulphonic acids or by the combination of equimolecular quantities of the amine-sulphonic acids and their diazo- compounds (Clayton Aniline Co., Eng. Pat. 14207, 1889; Bayer and Co., Eng. Pat. 18354, 1889). The mixture of dehydrothiotoluidine sulphonic acid and primuline sulphonic acid, obtained by sulphonation of the crude primuline melt as above described, is suspended in water and neutralised with ammonia. To the solution of the mixed ammonium salts is then added one half of the quantity of sodium nitrite necessary for complete diazotisation (as determined by titration with a standard nitrite solution). Dilute hydrochloric acid is then run in until the mixture is acid to Congo paper. After stirring for half an hour to complete the diazotisation, sodium carbonate is slowly added during 2 or 3 hours until the mixture is just alkaline. After standing over-night, a further quantity of sodium carbonate is added and the mixture is slowly heated up to 70° by admission of steam. The colouring-matter is then salted out by addition of sufficient common salt, filtered off, dried and ground.

Clayton Yellow dyes cotton directly from a boiling bath in strong bright greenish-yellow shades, which render it valuable for admixture with other salt dyestuffs. It is, however, not fast to alkalis, acids or light. The dyestuff, both in substance and upon the fibre, is changed to orange-red by caustic alkalis. Hot aqueous acids decompose it with regeneration of the respective diazo compounds.

By employment of the pure ammonium salt of dehydrothiotoluidine sulphonic acid instead of the mixture with primuline, a greener brand of Clayton Yellow is obtained, which has the constitution:—

$$CH_3{\cdot}C_6H_3{<}\begin{matrix}N\\S\end{matrix}{>}C{\cdot}C_6H_3(SO_3Na)N_2$$

$$CH_3{\cdot}C_6H_3{<}\begin{matrix}N\\S\end{matrix}{>}C{\cdot}C_6H_3(SO_3Na)NH$$

Nitrophenine Yellow is a mixture of the compounds $D{\cdot}NH{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$ and

$$P{\cdot}NH{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$$

obtained by combining diazotised *p*-nitraniline with dehydrothiotoluidine sulphonic acid and primuline (Clayton Aniline Co., Eng. Pat. 24870, 1893).

A solution of *p*-nitrodiazobenzene chloride obtained by diazotising 180 lbs. of *p*-nitraniline by means of 100 lbs. of sodium nitrite and 43 gals. of hydrochloric acid is run slowly into a cold solution in about 1000 gals. of water containing the sodium salts of the mixed sulphonic acids, obtained by sulphonation of the crude primuline melt, in quantity equivalent to 98 lbs. of sodium nitrite, and rendered alkaline by addition of 300 lbs. of dry sodium carbonate. After stirring for some time the mixture is left over-night. It is then heated to about 80° by introduction of steam and the dyestuff salted out with common salt, pressed and dried.

Nitrophenine dyes cotton directly in pure yellow shades, which, however, are very deficient in fastness to light, alkalis and acids. Caustic soda changes the shade to violet. It is now but little used.

Chloramine Yellow (Syn. Oxyphenine, Diamine Fast Yellow B, Columbia Yellow). These dyestuffs are mixtures of the azo compounds, $D{\cdot}N_2{\cdot}D$, $D{\cdot}N_2{\cdot}P$, and $P{\cdot}N_2{\cdot}P$, prepared by oxidation with sodium hypochlorite of an

alkaline solution of the mixed sodium sulphonates obtained from the crude primuline melt (Fr. Pat. 209519, 1890; Eng. Pats. 19061, 1891; 5761, 1892; 22914, 1884).

The dyestuffs, **Chlorophenine Y** and **Diamine Fast Yellow 2F**, are obtained in similar manner from the pure dehydrothiotoluidine-sulphonate, and therefore have the constitution :—

$$CH_3\cdot C_6H_3\!<\!\begin{matrix}N\\S\end{matrix}\!>\!C\cdot C_6H_3(SO_3Na)\cdot N$$
$$\|$$
$$CH_3\cdot C_6H_3\!<\!\begin{matrix}N\\S\end{matrix}\!>\!C\cdot C_6H_3(SO_3Na)\cdot N$$

For their preparation, 500 lbs. of ammonium dehydrothiotoluidine sulphonate is boiled in a lead-lined vat with 500 gals. of water containing caustic soda in small excess until all the ammonia has been expelled. When cold, the solution is diluted to 1000 gals. and 230 gals. of sodium hypochlorite solution (equals 10 p.c. active chlorine) are added. After standing over-night, the mixture is heated slowly by admission of steam, and is finally kept at 75°–80° until all chlorine has disappeared and the solution no longer reacts with starch iodide paper. The colour of the mixture is at first a dull yellow, but finally becomes a bright yellowish-orange. The colouring-matter is then salted out, pressed and dried.

It dyes cotton directly from a neutral bath in yellow shades which are unaffected by alkalis and acids and are extremely fast to light and chlorine. It is not discharged by reducing agents.

Thioflavine T (trimethyldehydrothiotoluidine chloride)

$$CH_3\cdot C_6H_3\!<\!\begin{matrix}CH_3\\S\end{matrix}\!>\!\begin{matrix}N\\C\cdot C_6H_4\cdot N(CH_3)_2\end{matrix}\!<\!Cl$$

Prepared by heating dehydrothiotoluidine base with methyl alcohol and hydrochloric acid for several hours under pressure at 160°–170° (A. G. Green and T. A. Lawson, Chem. Soc. Trans. 1889, 55, 230; Cassella & Co., Eng. Pats. 6319, 1888; 14884, 1888; J. Soc. Chem. Ind. 1890, 54; Dyers and Colourists, 1889, 106). In place of pure dehydrothiotoluidine, the mixture of this base with primuline base can be used, which is obtained by heating *p*-toluidine (2 mols.) with sulphur (4 atoms). In the latter case, dimethyl-primuline base is formed simultaneously and remains undissolved when the melt is extracted with boiling water. On adding salt to the hot solution, the dyestuff separates as a yellow crystalline precipitate. Thioflavine T is a basic colouring-matter which dyes tannin mordanted cotton in pure greenish-yellow shades. It also dyes silk a pure yellow with greenish fluorescence. It is faster than Auramine to acids, alkalis, and high temperatures, and since, like other members of the thiazol series, it is not affected by reducing agents, it also finds employment as a 'discharge' colour in calico-printing.

Thioflavine S is a dimethyl derivative of primuline obtained by the action of fuming sulphuric acid upon the portion insoluble in water of the product of methylation of crude primuline base (Cassella & Co., Eng. Pats. 6319, 1888; 14884, 1888; J. Soc. Dyers Cols. 1889, 106).

Thioflavine S dyes cotton directly in bright greenish-yellow shades, not affected by alkalis, although rather sensitive to light. It is fast to chlorine and is not discharged by reducing agents.

Substantive Azo Dyestuffs derived from Dehydrothiotoluidine Sulphonic Acid and from Primuline.

The following compounds which dye cotton directly are prepared from the diazo derivatives of dehydrothiotoluidine sulphonic acid, or of the mixture of the latter with primuline, by combination with the respective components.

Dianil Yellow $D—N_2—CH\!<\!\begin{matrix}CO\cdot CH_3\\CO\cdot OC_2H_2\end{matrix}$ is obtained from the diazo derivative and acetoacetic ester (Eng. Pat. 17328, 1897).

Oriol Yellow (Syn. Cotton Yellow R, Alkali Yellow) $D—N_2—C_6H_3(OH)CO_2H$ is obtained from the diazo derivative and salicylic acid (D. R. P. 48465, 1888).

Benzo Brown 5R (Syn. Alkali Brown) $D—N_2—C_6H_3(NH_2)_2$ is obtained from the diazo derivative and *m*-phenylenediamine. It dyes cotton reddish-brown.

Atlas Red $D—N_2—C_6H_2(CH_3)(NH_2)_2$ is obtained from the diazo derivative and *m*-toluylenediamine (Eng. Pat. 10448, 1890). Dyes cotton in terra-cotta shades, and gives browns upon diazotisation and development.

Cotton Yellow G

$$D—N_2—C_6H(SO_3Na)_2(NH_2)_2$$

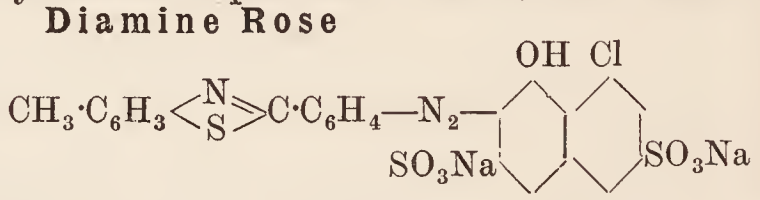
is obtained from the diazo compound and *m*-phenylenediamine-di-sulphonic acid (1 : 3 : 4 : 6) (Eng. Pat. 14678, 1893). It dyes cotton in orange-yellow shades.

Rosophenine 10B

$$D—N_2—C_{10}H_5(OH)SO_3Na$$

is obtained from the diazo derivative and α-naphthol-*p*-sulphonic acid (N. and W. acid). It dyes cotton in pink to red shades, fast to acids.

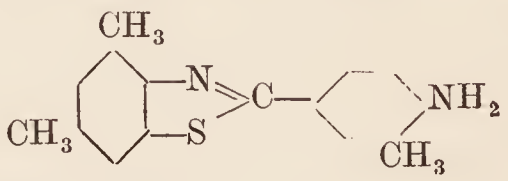
Diamine Rose



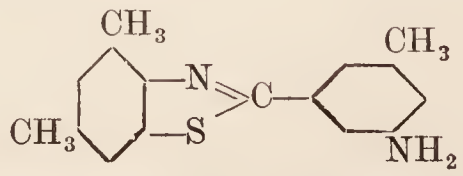
This dyestuff is obtained by combining the diazo compound of dehydrothiotoluidine (base) with 1 : 8-chloronaphthol-3 : 6-disulphonic acid. It dyes cotton directly in rose-pink shades.

Substantive Azo Dyestuffs derived from Dehydrothioxylidines.

By heating *m*-xylidine (6 parts) with sulphur (1 part) to the boiling-point until evolution of hydrogen sulphide ceases, a mixture is obtained consisting of dehydrothioxylidine



and the isomeric base



The first forms small yellowish-white prisms of

m.p. 107°, the second melts at 121°. After removal of the excess of *m*-xylidine by distillation, the two bases are separated by means of aqueous hydrochloric acid (30 p.c. HCl) in which the *iso*-base is insoluble (Anschütz and Schultz, Ber. 1889, 22, 582; Paul, Zeitsch. angew. Chem. 1896, 22; J. Soc. Chem. Ind. 1897, 730).

Erica B

$$C_6H_2(CH_3)_2\langle{}^{N}_{S}\rangle C\cdot C_6H_3(CH_3)N_2\cdot C_{10}H_4(OH((SO_3Na)_2$$

is obtained by combining the diazo compound of dehydrothioxylidine with the α-naphthol-3 : 8-disulphonic acid (ε- acid) (Berlin Aniline Co., Eng. Pat. 1733, 1888). It dyes cotton directly in brilliant pink shades of good fastness to washing and fairly resistant to light.

Salmon Red

$$C_6H_2(CH_3)_2\langle{}^{N}_{S}\rangle C\cdot C_6H_3(CH_3)N_2\cdot C_{10}H_4\langle{}^{(SO_3Na)_2}_{NH_2}$$

is obtained by combining the diazo compound of dehydrothioxylidine with β-naphthylamine-3 : 6-disulphonic acid (amino-R-acid). It yields bright salmon shades on unmordanted cotton. The Geranines also belong to the same class.

Emin Red

$$C_6H_2(CH_3)_2\langle{}^{N}_{S}\rangle C\cdot C_6H_3(CH_3)N_2\cdot C_{10}H_5(OH)SO_3Na$$

is obtained by combining the diazo- compound of *iso*dehydrothioxylidine with β-naphthol-6-sulphonic acid (Schaeffer acid). It dyes wool red from an acid bath but has little affinity for cotton. A. G. G.

PRINCE'S METAL or **PRINCE RUPERT'S METAL.** A brass containing about 25 p.c. of zinc.

PRINTER'S IRON LIQUOR. *Ferrous acetate v.* Acetic acid.

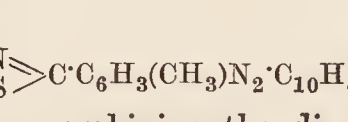
PROCAINE. Syn. for Novocaine.

PRODUCER GAS *v.* Fuel.

PROFERRIN. Iron nucleo proteid.

PROFLAVINE. 3-6-diamino acridine sulphate $C_{13}H_{11}N_3H_2SO_4,H_2O$, a reddish-brown powder, used as an intravenous antiseptic. *V.* Acridine Dyestuffs.

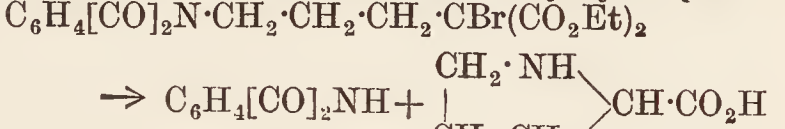
PROLINE, *pyrrolidine-2-carboxylic acid*



discovered by Fischer among the products of hydrolysis of casein (Zeitsch. physiol. Chem. 1901, 33, 151; Ber. 1902, 35, 227), is a common constituent of the product of proteid hydrolysis, occurring in quantities varying from 11 p.c. in salmin (Kossel and Dakin, Zeitsch. physiol. Chem. 1904, 41, 407) to 1 p.c. and under in silk fibroin (Fischer, *ibid.* 1903, 39, 155; Abderhalden and others, *ibid.* 1909, 61, 259; 62, 129, 131, 142; 1910, 64, 460), *v.* Proteins. It is a product of the digestion of gliadin (Fischer and London, *ibid.* 1911, 73, 398); 0·5 gram of proline as the hydantoin was obtained from the intestine of five dogs (Abderhalden and Kautzsch, *ibid.* 1912, 78, 96). By means of a new method of extraction, using butyl alcohol as the solvent, Dakin found 8 p.c. proline among th products of hydrolysis of caseinogen (Bio-Chem. J. 1918, 12, 290). It has also been isolated from the etiolated seedlings of *Vicia sativa* (Linn.) and *Lupinus albus* (Linn.) (Schulze and Winterstein, *ibid.* 1905, 45, 38); *v.* Kossel and Edlbacher (Zeitsch. physiol. Chem. 1915, 94, 264) and Meisenheimer (Wechschr. f. Brauerei, 32, 325) for its presence in the echinoderm and yeast cell. It was shown by Fischer and Abderhalden (*ibid.* 1903, 39, 81; 45, 215), Fischer and Boehner (*ibid.* 1910, 65, 118) that proline is a primary product of protein hydrolysis, and not, as suggested by Sörensen (Chem. Zentr. 1905, ii. 398), a secondary product arising from α-amino-δ-hydroxyvaleric acid, since it is formed when the hydrolysis is effected by pepsin hydrochloric acid or pancreatin as well as by acids, caustic alkali, or barium hydroxide; whereas α-amino-δ-hydroxyvaleric acid has not been obtained by hydrolysis of proteins, and, moreover, does not yield proline by treatment with barium hydroxide.

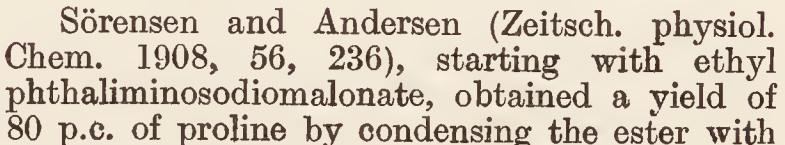
Synthesis.—Pyrrolidine-2-carboxylic acid was first synthesised by Willstätter (Ber. 1900, 33, 1160) from ethyl γ-bromopropylmalonate; this yields with bromine ethyl γ-bromopropylbromomalonate, which on treatment with ammonia and subsequent hydrolysis is converted into pyrrolidine-2-carboxylic acid

$$CH_2Br\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2 \rightarrow CH_2Br\cdot CH_2\cdot CH_2\cdot CBr(CO_2Et)_2$$



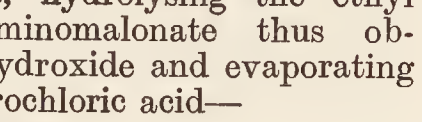
Fischer (Ber. 1901, 34, 454) obtained it in a similar manner from γ-phthaliminopropylmalonate: the bromo derivative of this compound when treated with ammonia gave a complex product from which phthalimide and pyrrolidine-2-carboxylic acid were obtained by hydrolysis

$$C_6H_4[CO]_2N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CBr(CO_2Et)_2$$



Sörensen and Andersen (Zeitsch. physiol. Chem. 1908, 56, 236), starting with ethyl phthaliminosodiomalonate, obtained a yield of 80 p.c. of proline by condensing the ester with trimethylene bromide, hydrolysing the ethyl γ-bromopropylphthaliminomalonate thus obtained with sodium hydroxide and evaporating the product with hydrochloric acid—

$$C_6H_4[CO]_2N\cdot CNa(CO_2Et)_2 \rightarrow C_6H_4[CO]_2N\cdot C(CO_2Et)_2CH_2\cdot CH_2\cdot CH_2Br \rightarrow CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot C(CO_2Na)_2CH_2\cdot CH_2\cdot CH_2OH$$



A further synthetic method due to Fischer and Zemplén (Ber. 1909, 42, 1022) consists in oxidising benzoylpiperidine with potassium permanganate into δ-benzoylaminovaleric acid $COPh\cdot NH[CH_2]_4CO_2H$, which with bromine and red phosphorus yields α-bromo-δ-benzoylaminovaleric acid, and this when boiled with hydrochloric acid yields proline in quantity.

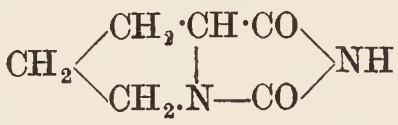
The proline obtained from proteins is optically active and consists of a mixture of the lævo and racemic forms; the synthetic product is, of course, the racemic compound, but by a modification of the last method of synthetic preparation, Fischer and Zemplén (*ibid.* 2989) obtained both *d*- and *l*-proline, for this purpose *m*-nitrobenzoylproline obtained as above from *m*-nitrobenzoylpiperidine was resolved into its

optically active constituents by means of the cinchonine salt, and these on hydrolysis with hydrochloric acid are decomposed into *m*-nitrobenzoic acid and the optically active prolines.

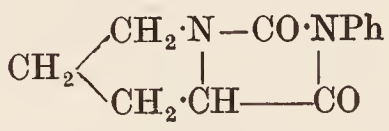
l-**Proline**, the natural product, crystallises in flat needles, m.p. 206°–209°, with decomposition (Fischer, Zeitsch. physiol. Chem. 1901, 33, 151), 220°–222° (Kossel and Dakin, *ibid.* 1904, 41, 407), readily soluble in water or alcohol, insoluble in ether; it has a sweet taste; $[\alpha]_D^{20°}$ −77·40° in aqueous solution. The synthetic preparation has m.p. 215°–220°, $[\alpha]_D^{20}$ −80·4° (±0·5°) (Fischer, Ber. 1909, 42, 2989). The *copper* salt $C_{10}H_{16}O_4N_2Cu$ forms large dark blue soluble plates; l-*prolylchloride hydrochloride*

$$C_4H_8N{\cdot}COCl{\cdot}HCl$$

is prepared by the action of phosphorus pentachloride on *l*-proline (Fischer and Reif, Annalen, 1908, 363, 118); l-*prolylhydantoin*



has m.p. 165°–167°, $[\alpha]_D^{20°}$ −232° to −238·5°, (Dakin, Bio-Chem. J. 1918, 12, 290); the *phenyl*-iso*cyanate* yields the *anhydride* or *phenylhydantoin*



m.p. 144° (corr.), soluble in 110 parts of hot water (Fischer, Zeitsch. physiol. Chem. 1901, 33, 151); the *β-naphthalenesulphonic derivative*

$$\begin{matrix} CH_2{\cdot}N{\cdot}SO_2{\cdot}C_{10}H_7 \\ | \qquad\quad >CH{\cdot}CO_2H,H_2O, \\ CH_2{\cdot}CH_2 \end{matrix}$$

m.p. 133·7° (corr.); the anhydrous substance melts at 136°, soluble in 130 parts of boiling water; the *picrate* $C_{11}H_{12}O_9N_4$, m.p. 153°–154°, crystallises in needles from alcohol, and is less soluble than the corresponding salt of the racemic compound (Alexandroff, *ibid.* 1905, 46, 17).

d-**Proline** crystallises in prisms, m.p. 215°–220°, with decomposition, has $[\alpha]_D^{20°}$ +81·9°; the *copper salt* closely resembles the corresponding salt of *l*-proline; the m-*nitrobenzoyl* derivative $C_{12}H_{12}O_5N_2$ has m.p. 137°–140°; $[\alpha]_D^{20°}$ +120° (Fischer and Zemplén, Ber. 1909, 42, 2992).

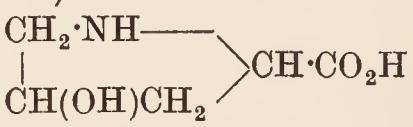
dl-**Proline** forms small prisms, m.p. 205° (with decomposition); and is converted by the action of putrefying bacteria into δ-aminovaleric acid and *n*-valeric acid (Ackermann, Zeitsch. Biol. 1911, 57, 104; Neuberg, Biochem Zeitsch. 1911, 37, 490). The *copper salt* $C_{10}H_{16}O_4N_2Cu,2H_2O$, sky-blue plates or prisms, become violet when anhydrous; sparingly soluble in water, insoluble in alcohol. For the identification of *dl*-proline by means of its copper calt, *v.* Fischer and Gerlach (Ber. 1912, 45, 2543), and Gluud (Chem. Soc. Proc. 1913, 29, 177). The m-*nitrobenzoyl* derivative has m.p. 90°–92° and is soluble in 40 parts of hot water; the *phenyl*isocyanate derivative melts at about 170° with decomposition, forming the *hydantoin* $C_{12}H_{12}O_2N_2$, m.p. 118° (corr.) (Fischer, Ber. 1901, 34, 454); the *picrate* $C_{11}H_{12}O_9N_4$, forms small yellow indefinite crystals, m.p. 135°–137°, readily soluble in hot water (Alexandroff, Zeitsch. physiol. Chem. 1905, 46, 17).

For the biological value of proline, *v.* Abderhalden (Zeitsch. physiol. Chem. 1915, 96, 1–147; Sure, J. Biol. Chem. 1920, 43, 443; 1921, 46, 443); for the fate of proline in the animal body, *v.* Dakin (J. Biol. Chem. 1913, 13, 513); and for the preparation and properties of polypeptides containing the *prolyl* radicle, *v.* Fischer and Abderhalden (Ber. 1904, 37, 3071; Fischer and Reif, Annalen, 1908, 363, 118; Fischer and Luniak, Ber. 1909, 42, 4752).

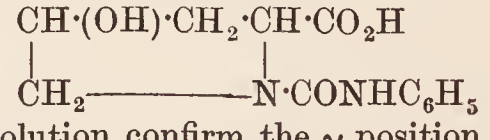
Estimation.—Proline occurs in that fraction of the esterified product of protein hydrolysis that is soluble in alcohol; and as it does not give up its nitrogen with nitrous acid as do the esters of the amino acids that distil over with it, the amount of proline present in the mixture is measured by the difference between the total nitrogen content of the mixture, and the nitrogen evolved on treating the mixture with nitrous acid (van Slyke, J. Biol. Chem. 1911, 9, 205); but there is no satisfactory method at present for estimating the amount of pure proline contained in the decomposition products of a protein (Abderhalden and Kautzsch, Zeitsch. physiol. Chem. 1912, 78, 96).

Oxyproline, *hydroxyproline*, *hydroxypyrrolidine-2-carboxylic acid* $C_5H_9O_3N$ was isolated by Fischer (Ber. 1902, 35, 2660) from the hydrolysis product of gelatin, and is formed by the hydrolysis of other proteins (*cp.* Levene and Beatty, Zeitsch. physiol. Chem. 1906, 49, 252; Abderhalden, *ibid.* 1903, 37, 484, 499; Abderhalden and Rona, *ibid.* 1904, 41, 278).

Leuchs, Leuchs and Bormann (Ber. 1905, 38, 1937; 1919, 52, 2086) prepared synthetically three γ-hydroxyprolines (4-*hydroxypyrrolidine*-2-*carboxylic acid*)



of which the stereoisomerides are of the natural hydroxyproline; the synthesis of 4-hydroxypyrrolidine-1-phenylisocyanate



and its resolution confirm the γ position of the hydroxyl group: the synthetic *l*-γ-hydroxyproline sodium salt has $[\alpha]_D^{20°}$ −37·0°, whereas the natural product has $[\alpha]_D^{19°}$ −37·2°, synthetic *l*-hydroxyproline has $[\alpha]_D^{20°}$ −76·3° (Leuchs and Brewster, *ibid.* 1913, 46, 986; Leuchs and Felser, Ber. 1908, 41, 1726); 4-hydroxy-benzoyl proline has m.p. 158°–161° (Hammarsten Compt. rend. Lab. Carlsberg, 1916, 11, 223); *d*-hydroxyproline has m.p. 274°, $[\alpha]_D^{21°}$ +75·2°.

l-Oxyproline crystallises in colourless rhombic plates, m.p. 270°, with decomposition, readily soluble in water, less so in alcohol; it has a very sweet taste, $[\alpha]_D^{20°}$ −81·04°; *cf.* Leuchs and Brewster (*l.c.*). It is converted into *dl*-proline by reduction with hydrogen iodide and phosphorus. The *copper* salt

$$(C_5H_8O_3N)_2Cu,4H_2O$$

forms deep blue needles, readily soluble in water, insoluble in alcohol; the *phenyl*isocyanate

$C_{12}H_{14}O_4N_2$ has m.p. 175°; the *β-naphthalene-sulphonic* derivative $C_{15}H_{15}O_5NS,H_2O$ becomes anhydrous at 85°, m.p. 91°–92° (corr.), soluble in 25 parts of hot water. M. A. W.

PROOF SPIRIT *v.* ALCOHOL.

PROPALDEHYDE $C_2H_5{\cdot}CHO$ is best prepared by the oxidation of propyl alcohol with chromic acid mixture (Marchionneschi, Gazz. chim. ital. 1907, 37, ii. 201; Lieben and Zeisel, Monatsh. 1883, 4, 14; Przybytek, J. Russ. Phys. Chem. Soc. 1876, 8, 335; Chancel, Annalen, 1869, 151, 301). It can also be obtained by heating propylene glycol with water at 220° (Linnemann, *ibid.* 1878, 192, 61), or, together with acetone, by using propylene dichloride (Linnemann, *ibid.* 1872, 161, 64); hydrogen peroxide in presence of an iron salt (Neuberg and Rewald, Biochem. Zeitsch. 1915, 71, 158). By the distillation of raw sugar with lime, propaldehyde is obtained, together with other products (E. Fischer and Laycock, Ber. 1889, 22, 105).

Properties.—Propaldehyde is a liquid having a penetrating smell; b.p. 48·8° (corr.) (Linnemann, Annalen, 1872, 161, 22; *cf.* Rossi, *ibid.* 159, 79); sp.gr. 0·80648 at 15°, 0·79664 at 25° (Perkin, Chem. Soc. Trans. 1884, 476; *cf.* Brühl, Annalen, 1880, 203, 13; 0·8171 $\frac{19}{19}$, Harries and Oppenheim, Chem. Zentr. 1916, ii. 991; Pierre and Puchot, *ibid.* 1870, 155, 362; 1872, 163, 273); heat of combustion (const. press.) 434·35 cals. (Berthelot and Délepine, Compt. rend. 1900, 130, 1045); dielectric constant (Drude, Zeitsch. physikal. Chem. 1897, 23, 308); soluble in 5 vols. of water at 20°. Hydrogenation converts it into *n*-propyl alcohol. By passing ammonia into a well-cooled solution of propaldehyde, *propaldehyde ammonia* is produced (Waage, Monatsh. 1883, 4, 708), decomposes at 0°. Concentrated potassium hydroxide solution polymerises propaldehyde to *propionaldol*

$$CH_3{\cdot}CH_2{\cdot}CH(OH)CH(CH_3)CHO$$

(Thalberg, *ibid.* 1898, 19, 154). Propaldehyde condenses with other aldehydes to form *aldols*, *e.g.* with acetaldehyde to yield the aldol

$$CH_3{\cdot}CH(OH)CH(CH_3)CHO$$

(Schmalzhofer, *ibid.* 1900, 21, 671; Kohn, *ibid.* 1901, 22, 21), but with formaldehyde the aldol is not obtained, the product being *αα*-dimethylolpropaldehyde

$$CHO{\cdot}CH(CH_3)CH_2{\cdot}OH$$

(Koch and Zerner, *ibid.* 443). By the action of aniline on a mixture of propaldehyde and acetaldehyde, *αβ*-dimethylquinoline, *α*-ethyl-*β*-methylquinoline, and quinaldine are formed (Rohde, Ber. 1887, 20, 1911). It combines with hydrogen cyanide to form *α*-hydroxybutyronitrile (*α*-cyanopropaldehyde) (Henry, Bull. Acad. roy. Belg. [iii.] 35, 133). Propaldehyde, sodium succinate, and acetic anhydride react at 110°–120°, yielding ethylparaconic acid (Fittig and Delisle, Annalen, 1889, 255, 56). With phenylpyrrole it forms $C_{13}H_{13}N$ (Colaciechi and Bertoni, Atti R. Accad. Lincei, 1912, [v.] 21, i. 600.

Detection.—If propaldehyde is warmed with twice its volume of phenylhydrazine, the product washed with dilute acetic acid and filtered, then, on heating with an equal quantity of zinc chloride at 180°, scatole is produced (E. Fischer, Ber. 1889, 22, 104).

Parapropaldehyde and **metapropaldehyde.** These two compounds, each of which has the formula $C_9H_{18}O_3$, are produced by passing a few bubbles of hydrogen chloride through a solution of propaldehyde cooled in a freezing mixture. After standing for some time the metapropaldehyde, which is a light crystalline solid (m.p. 80°), is filtered off. The filtrate is distilled under 50 mm. pressure, and the parapropaldehyde obtained as a colourless liquid lighter than water; b.p. 85°–86°/50 mm.; 169°–170° (corr.), and changing at that temperature into propaldehyde. At −20° it solidifies to a mass of colourless needles. By heating either of these compounds with a little hydrochloric or sulphuric acid, propaldehyde is formed, together with a little tarry matter (Orndorff, Amer. Chem. J. 1890, 12, 352; Orndorff and Balcom, *ibid.* 1894, 16, 647). Parapropaldehyde is also formed by adding 200 grms. of ethyl chloracetate and some zinc to 100 grms. of propaldehyde, and allowing the mixture to stand for some months (Reformatsky, J. Russ. Phys. Chem. Soc. 1890, 22, 197). For action of bromine on parapropaldehyde, *v.* Franke, Annalen, 1907, 351, 421.

In these two polymerides union of the three molecules of propaldehyde probably takes place through the oxygen atoms, and metapropaldehyde and parapropaldehyde are probably examples of *cis-trans* isomerism (Orndorff and Balcom, *l.c.*).

PROPÆSIN. Trade name for the propyl ester of *p*-aminobenzoic acid.

PROPÆSIN; PROPONAL *v.* SYNTHETIC DRUGS.

PROPIOLIC COMPOUNDS. From propiolic acid, $HC{:}C{\cdot}COOH$, may be derived a series of acids of the general formula $C_nH_{2n+1}{\cdot}C{:}C{\cdot}COOH$, and the members of this series may be regarded as the true homologues of propiolic acid, although the isomeric acids, in which the acetylene linkage is not in the *α-β* position, are often also described as propiolic compounds. The alkyl group may be replaced by an aromatic radicle, *e.g.* in phenyl propiolic acid $C_6H_5{\cdot}C{:}C{\cdot}COOH$, the nitro-derivative of which is important as being the initial substance in Baeyer's original synthesis of indigo.

Alkylpropiolic acids $R{\cdot}C{:}C{\cdot}COOH$. Methods of formation:

1. By the action of carbon dioxide on the sodium acetylenes—

$$R{\cdot}C{:}CNa+CO_2=R{\cdot}C{:}C{\cdot}COONa$$

A convenient modification of this synthesis is to employ chlorocarbonic ester and saponify the product—

$$R{\cdot}C{:}C{\cdot}Na+Cl{\cdot}COOC_2H_5=NaCl+R{\cdot}C{:}C{\cdot}COOC_2H_5$$

(Moreu and Delange, Compt. rend. 1903, 136, 552).

2. By the action of dilute aqueous potash on the chloro derivatives of the acrylic acids—

$$R{\cdot}CCl{:}CH{\cdot}COOH-HCl=R{\cdot}C{:}C{\cdot}COOH$$

Reactions.—1. On reduction with sodium amalgam the corresponding fatty acid is obtained.

2. On boiling with alcoholic potash *β*-ketonic acids are formed—

$$R{\cdot}C{:}C{\cdot}COOH+H_2O=R{\cdot}CO{\cdot}CH_2{\cdot}COOH$$

(Moreu and Delange, Compt. rend. 1902, 136, 733).

3. On heating with aqueous potash a ketone is obtained—

$$R{\cdot}C{:}C{\cdot}COOH+H_2O=R{\cdot}CO{\cdot}CH_3+CO_2$$

4. The propiolic esters react readily with alcohols and amines, forming addition compounds, and also with hydrazine forming pyrazole derivatives (Moreu and Lazennec, Compt. rend. 1906, 143, 596, and 1239).

Propiolic acid, propargylic acid,

$$H{\cdot}C{:}C{\cdot}COOH$$

was discovered by Bandrowski, who obtained it by warming the aqueous solution of the acid potassium salt of acetylene dicarboxylic acid. It is a colourless liquid, slightly heavier than water, with a strong smell of acetic acid, freely soluble in water and organic solvents, m.p. 9°, b.p. 140°–145° (decomposition). Propiolic acid is a stronger acid than acetic acid, which is attributed to the negative nature of the acetylene linkage. Its alkali and alkaline earth salts are characterised by excessive solubility in water; on boiling their solutions there is gradual decomposition

$$2HC{:}C{\cdot}COOK=K_2CO_3+CO_2+2C_2H_2$$

Owing to the fact that there is an acetylene hydrogen atom present, propiolic acid, its salts and esters are capable of forming characteristic metallic derivatives, such as

$$AgC{:}C{\cdot}COOC_2H_5,\ CuC{:}C{\cdot}COONa,\ \&c.$$

The copper compound on oxidation with potassium ferricyanide yields a propiolic derivative containing two acetylene linkages

$$(\cdot C{:}C{\cdot}COOH)_2$$

and by the elimination of a carboxyl group and the subsequent oxidation of the copper compound of the substance thus obtained, Baeyer was able to perform a synthesis of the acid $(\cdot C{:}C{\cdot}C{:}C{\cdot}COOH)_2$, containing four acetylene linkages (Ber. 1885, 18, 2269).

Propiolic alcohol, propargyl alcohol,

$$CH{\equiv}C{\cdot}CHO_2H$$

obtained by treating allyl debromide with alcoholic potash. B.p. 115°. Gives a yellow precipitate with ammoniacal cuprous chloride.

Propiolic aldehyde $HC{:}C{\cdot}CHO$ has been obtained by Claison (Ber. 1898, 31, 1022; 1903, 36, 3664) from the acetal of dibromoacrolein by converting it into propiolic acetal by the action of potash and then eliminating the ethoxyl group by means of dilute sulphuric acid. It is a colourless mobile liquid, b.p. 60°, with an even more pungent odour than acrolein. Like propiolic acid, it forms silver and copper derivatives. The aldehyde group is attached to the acetylene nucleus even less firmly than the carboxyl in propiolic acid, cold aqueous alkalis causing immediate decomposition—

$$HC{:}C{\cdot}CHO+KOH=C_2H_2+H{\cdot}COOK$$

Similarly hydroxylamine and phenylhydrazine do not condense normally, but yield cyclic products, namely isoxazole and pyrazole.

Propiolamide $HC{\equiv}C{\cdot}CONH_2$, m.p. 62°, gives a silver and cuprous derivative.

Methylpropiolic acid $CH_3{\cdot}C{:}C{\cdot}COOH$, m.p. 76°, b.p. 203°. The esters of this acid and the higher homologues find some application in the preparation of artificial perfumes (Moreu, D. R. PP. 133631; 158252).

Phenylpropiolic acid $C_6H_5{\cdot}C{:}C{\cdot}COOH$, has been obtained by the action of sodium and carbon dioxide on bromophenylacetylene, $C_6N_5{\cdot}C{:}CBr$; by the action of carbon dioxide on sodium phenylacetylene $C_6H_5{\cdot}C{:}CNa$; by the action of alcoholic potash on bromocinnamic acid or on phenyldibromopropionic acid. White crystals slightly soluble in water, m.p. 137°; it forms soluble salts, the sodium salt having strong disinfecting properties (Kozai, Chem. Zentr. 1906, i. 1758). Reactions: On heating it loses carbon dioxide and forms phenylacetylene; chromic anhydride oxidises it to benzoic acid; on reduction with zinc dust and acetic acid cinnamic acid is formed; bromine is added readily with the production of two isomeric dibromo-cinnamic acids; acetic anhydride causes condensation to a phenylnaphthalene derivative (Bucher, J. Amer. Chem. Soc. 1910, 32, 212).

***o*-Nitrophenylpropiolic acid**

$$C_6H_4(NO_2){\cdot}C{:}C{\cdot}COOH$$

(*see* INDIGO, ARTIFICIAL) was first obtained by Baeyer, who utilised it in the synthesis of indigo. On nitrating cinnamic acid the ortho-derivative is obtained; if this is converted into the dibromo acid by the addition of bromine and the product treated with alkali, *o*-nitrophenylpropiolic acid results (Baeyer, Ber. 1880, 13, 2258; D. R. P. 11857). On reduction in alkaline solution, it gives first *isatogenic acid*, and then loses carbon dioxide to form indigo; or by heating it may be converted by loss of carbon dioxide into *o*-nitrophenylacetylene, the copper compound of which may be oxidised by potassium ferricyanide to the diacetylene derivative, and this on reduction yields indigo. On treating with alkalis *o*-nitrophenylpropiolic acid forms isatin; by the action of concentrated sulphuric acid, isatogenic acid (Baeyer, D. R. P. 17656); on treatment with sulphuric acid containing ferrous sulphate, indoin (Bayer, D. R. PP. 12601; 14997); by reduction with ammonium sulphide, indoxylic acid (*ibid.* 17656); by the milder reducing action of zinc and ammonium hydroxide, homo-anthroxamic acid (Heller and Tischner, Ber. 1909, 43, 4555).

PROPION. Trade name for diethyl-ketone $(C_2H_5)_2{\cdot}CO$, used as a hypnotic and anæsthetic.

PROPIONIC ACID $CH_3{\cdot}CH_2{\cdot}COOH$. Discovered by Gottlieb (Annalen, 52, 121) in 1844 by oxidising metacetone, and termed by him *metacetonic acid*; he also obtained it by heating gum, sugar, starch, &c., with concentrated potash solution. It is produced in the fermentation of calcium lactate, tartrate, and malate, and also in the fermentation of glycerol (Fitz, Ber. 12, 476), and is found among the products of the distillation of wood. It may be prepared by heating the nitrile with dilute sulphuric acid (Beckurts and Otto, Ber. 10, 262), or by treating propyl alcohol with a mixture of potassium chromate and sulphuric acid (Pierre and Puchot, Ann. Chim. [iv.] 28, 45). Colourless liquid smelling like acetic acid; b.p. 140·7°, sp.gr. 0·9937 at 20·3°/20·3° (Perkin, Chem. Soc. Trans. 1896, 1172); 140·76° (corr.) (Thorpe and Rodger). Soluble in water, but on addition of calcium chloride to the solution it separates out as an oil.

Its vapour passed over thoria at 400°, or over manganese oxide at 450°, yields the corresponding ketone.

Methyl propionate boils at 79·5° (Kahlbaum, Ber. 1879, 344), and has sp.gr. 0·9387 at 0°/4° (Young and Thomas, Chem. Soc. Trans. 1893, 1219); **ethyl propionate** boils at 98·8°, and has sp.gr. 0·9124 at 0° (Schumann, Pogg. Ann. [2] 12, 41); 99·12°–99·22°, sp.gr. 0·8904 at 20°/4° (Matthews and Faville, J. Phys. Chem. 1918, 22, 1). **Propylpropionate**, b.p. 121·0–121·25; sp.gr. 0·8809 (Matthews and Faville (*l.c.*)).

PROPOLIS (*Bee-bread*, *Hive-dross*: Ger. *Vorwachs*, *Stopfwachs*). A resinous substance collected by bees from the outer surface of pollen granules. In the fresh condition propolis is soft and sticky, has a strong aromatic odour and a bitter taste, and varies in colour from greenish-yellow to brown. Below 15° it is brittle; m.p. 64°; sp.gr. 1·2 (Greshoff and Sach, Rec. trav. chim. 1903, 22, 139). It has been used in the treatment of rheumatism and gout (Brestowski, Handwörterbuch Pharm., II. 397).

Treatment with 95 p.c. alcohol extracts *propolis resin*, leaving *propolis wax* as residue. *Propolis balsam* is obtained from the resin by extraction with boiling light petroleum. It forms a non-irritant stopping for wounds and is highly prized as a varnish, since it dries to a brilliant film. On dry distallation the balsam is separated at 160° into a nearly colourless essential oil with a pronounced odour of hyacinths. If the distillation is continued up to 260° cinnamic acid passes over. The balsam contains about 10 p.c. of cinnamyl alcohol (Küstenmacher, Ber. deutsch. Pharm. Ges. 1911, 21, 65). *Cf.* Dieterich, Zeitsch. angew. Chem. 1911, 24, 1854.

Commercial propolis is much adulterated with bees-wax, and by the addition of metallic and other heavy insoluble impurities, but the freshly-collected substance has approximately the composition: Loss at 100°, water and essential oils, 5–6° p.c.; ash, 2·5 p.c.; insoluble residue, 12–13 p.c.; crude wax, 25–45 p.c.; propolis balsam, 3 p.c.; propolis resin, 55–65 p.c. (Dieterich, Chem. Zeit. 1910, 34, 1006).

Propolis resin is a brownish-black substance of the composition $C_{26}H_{26}O_6$. It is soft and very aromatic, and has m.p. 66°–67° and sp.gr. 1·186. It is soluble in ether, chloroform, or hot alcohol. By prolonged heating at 100° it becomes much harder.

PROPONAL. Trade name for dipropyl malonyl urea $(C_3H_7)_2C<^{CONH}_{CONH}>CO$, *v.* Pyrimidines and Synthetic Drugs.

PROPOSOTE. Syn. for creosote phenyl propionate.

PROPYL. A monovalent radicle yielding two types of compounds:—

(*a*) $CH_3{\cdot}CH_2{\cdot}CHX$, *normal.*

(*b*) $(CH_3)_2CHX$, *iso.*

Propane $CH_3{\cdot}CH_2{\cdot}CH_3$ occurs in crude petroleum (Ronalds, Zeitsch. Chem. 1865, 523; Lefebvre, *ibid.* 1869, 185). Prepared by heating acetone, glycerol, propionitrile, or allyl iodide with hydriodic acid (sp.gr. 1·8) at 280° (Berthelot, Bull. Soc. chim. [ii.] 7, 60; 9, 13, 184); by heating a mixture of methyl iodide and ethyl iodide with sodium under pressure; by the hydrogenation of propylene; by the interaction of *iso*propyl iodide with zinc and dilute sulphuric acid (Schorlemmer, Annalen, 150, 209), or with zinc and absolute alcohol (Frankland, Chem. Soc. Trans. 1885, 238); by heating propyl or *iso*propyl iodide with aluminium chloride at 130°–140° (Köhnlein, Ber. 1883, 16, 561; L. Meyer, *ibid.* 1894, 27, 2766; Kluge, Annalen, 282, 229), or by the action of sodamide on propyl iodide (Lebeau, Compt. rend. 1905, 140, 1042).

Propane is a colourless gas, a normal litre weighs 2·0200 grms. (Timmermans, J. Phys. Chem. 1920, 18, 133); heat of combustion (const. vol.) 528·4 Cal. (Berthelot and Matignon, Ann. Chim. [vi.], 30, 560), (const. press.) 553·5 Cal. (Berthelot, *l.c.*); ratio of specific heats 1·153 (Daniel, Bull. Soc. chim. 1899, [iii.] 21, 801); solubility in various solvents (Lebeau, Compt. rend. 1905, 140, 1454); illuminating power $1\frac{1}{2}$ times that of ethane (Frankland, Chem. Soc. Trans. 1885, 239). Propane condenses to a colourless liquid; b.p. −44·5° (760 mm.); solidifying at −187·8° (−189·9°, Maass and Wright); sp.gr. 0·536 at 0°/0°, 0·524 at 6·2°/6·2°, 0·520 at 11·5°/11·5°, 0·515 at 15·9°/15·9° (Hainlen, Annalen, 282, 245; L. Meyer, Ber. 1894, 27, 276; 1893, 26, 2071); b.p. −45° (1 atmo.), 0° (5 atmos.), 20° (8·8 atmos.), 43° (17·7 atmos.) (Olzewski, *ibid.* 1894, 27, 3306); b.p. −44·5° (757 mm.); crit. temp. 97·5°: crit. press. 45 atmos. (Lebeau, *l.c.*; Olzewski, *l.c.*; Hainlen, *l.c.*).

For its vapour pressure, *see* Burrell and Robertson (J. Amer. Chem. Soc. 1915, 37, 2188).

By the action of chlorine in the presence of iodine, the ultimate products are carbon tetrachloride and perchloroethane, formed by the action of excess of chlorine on the perchloropropane first formed (Krafft and Merz, Ber. 1875, 8, 1296).

For derivatives, *see* Branch and Titherley (Chem. Soc. Trans. 1912, 2349); Thorpe (*ibid.* 1912, 254); Wolff (D. R. P. 258473); Scholl and Egerer (Annalen, 1913, 397, 301); Longinov (J. Russ. Phys. Chem. Soc. 1914, 46, 1084).

Bromo Derivatives.

Propyl bromide, *α-bromopropane*

$CH_3{\cdot}CH_2{\cdot}CH_2Br$

Prepared by the action of hydrobromic acid on propyl alcohol (Linnemann, Annalen, 161, 40; Taboury, Bull. Soc. chim. 1911, [iv.] 9, 124).

B.p. 70·82° (corr.) (Brühl, *ibid.* 203, 13; *cf.* Zander, *ibid.* 214, 159); sp.gr. 1·3640 at 15°/15°, 1·3012 at 65·5°/65·5° (Perkin. Chem. Soc. Trans. 1896, 1237); b.p. 71·07° (corr.) (Thorpe); sp.gr. 1·3835 at 0° (Zander). By heating alone at 280°, or at a lower temperature with aluminium bromide, it is converted into *iso*propyl bromide (Aronstein, Ber. 1881, 14, 68; *cf.* Gustavson, J. Russ. Phys. Chem. Soc. 15, 61; Kekulé and Schrötter, Ber. 1879, 12, 2279; Michael and Leupold, Annalen, 1911, 379, 263); with aluminium bromide and benzene, cumene is formed (Gustavson, Ber. 1878, 11, 1251). Bromine alone yields propylene dibromide, whilst bromine and aluminium bromide yield dibromo-, tribromo-, and

tetrabromopropanes (Mouneyrat, Compt. rend. 1898, 127, 273).

*iso***Propyl bromide,** *β-bromopropane*

$CH_3{\cdot}CHBr{\cdot}CH_3$

Prepared by the action of hydrobromic acid on *iso*propyl alcohol at 150° (Linnemann, Annalen, 136, 41; Taboury, Bull. Soc. chim. 1911 [iv.] 9, 124); by heating propyl bromide (*q.v.*) with aluminium bromide; by the action of bromine on *iso*propyl iodide (R. Meyer, J. pr. Chem. [ii.] 34, 105); by heating propylene dibromide with hydriodic acid at 150° (Linnemann, Annalen, 161, 57).

B.p. 59°–59·5° (740 mm.); sp.gr. 1·3097 at 20°/4° (Brühl, *ibid.* 203, 13; *cf.* Přibram and Handl, Monatsh. 2, 646; Zander, Annalen, 214, 160), 59·73° (corr.) (Thorpe). Chlorine has no action in the cold; benzene and aluminium bromide yield cumene (Gustavson, Ber. 1878, 11, 1251).

Propylidene dibromide, *αα-dibromopropane* $CH_3.CH_2.CHBr_2$. Stated by Reboul (Ann. Chim. [v.] 14, 467) to be formed in small quantity, together with propylene dibromide, by the action of hydrobromic acid on *α*-bromopropylene; b.p. 130° (*circa*).

Propylene dibromide, *αβ-dibromopropane* $CH_3{\cdot}CHBr{\cdot}CH_2Br$. Prepared by the action of bromine on propylene (Reynolds, Annalen, 77, 120; Cahours, J. 1850, 496; Würtz, Annalen, 104, 244; Gladstone and Tribe, Chem. Soc. Trans. 1874, 408); by heating propyl bromide (Linnemann, Annalen, 161, 41; V. Meyer and Müller, Ber. 1891, 24, 4250), *iso*propyl bromide (Linnemann, Annalen, 136, 51), propyl or *iso*propyl chloride (Herzfelder, Ber. 1893, 26, 1260) with bromine in the presence of iron wire at 100°; together with trimethylene dibromide by heating propyl bromide and bromine at 45°–50° in the presence of aluminium bromide (Geromont, Annalen, 158, 370; Mouneyrat, Compt. rend. 127, 274).

B.p. 141·6° (corr.), sp.gr. 1·93326 at 20°/4° (Kahlbaum, Zeitsch. physikal. Chem. 26, 626, 646; *cf.* Zander, Annalen, 214, 175); b.p. 141·53° (corr.) (Thorpe). At 240°–250° it is partly converted into trimethylene dibromide (2–3 p.c.) (Faworsky and Sokownin, *ibid.* 354, 325); bromine and aluminium bromide yield *ααβ*-tribromo- and *ααβγ*-tetrabromopropane (Mouneyrat, Bull. Soc. chim. [iii.] 19, 805); alcoholic potash gives two isomeric bromopropylenes, and with excess of potash allylene. Zinc and acetic acid or sodium amalgam and alcohol yield propylene (Linnemann, Ber. 1877, 10, 1111); hydriodic acid gives *iso*propyl bromide (*q.v.*). By heating propylene dibromide with water, hydrobromic acid, propylene glycol, and a trace of acetone are formed (Niederist, Annalen, 196, 358); with water and lead oxide, acetone, propionaldehyde and propylene glycol are the products (Eltekow, J. Russ. Phys. Chem. Soc. 10, 212); with water and silver oxide propaldehyde is formed, but not propylene glycol (Beilstein and Wiegand, Ber. 1882, 15, 1497).

Trimethylene dibromide, *αγ-dibromopropane* $CH_2Br{\cdot}CH_2{\cdot}CH_2Br$. Prepared by saturating allyl bromide with hydrogen bromide at 30°–35° (Bruylants, Bull. Acad. roy. Belg. 1908, 1085; *cf.* Erlenmeyer, Annalen, 197, 180; Lermontoff, *ibid.* 182, 358; Roth, Ber. 1881, 14, 1351), or by heating it with hydrobromic acid at 150° (Bogomoleta, Bull. Soc. chim. [ii.] 30, 23; *cf.* Geromont, Annalen, 158, 370); by heating trimethylene glycol with fuming hydrobromic acid at 100° (Freund, Monatsh. 2, 639). To purify the trimethylene dibromide from the propylene dibromide, which is also formed in small amount, Gustavson (J. pr. Chem. [ii.] 59, 303) fractionally treats the product with zinc in alcoholic solution, the propylene dibromide being much more readily attacked than the trimethylene dibromide.

B.p. 162·25°; sp.gr. 2·017 at 0°/0°, 1·987 at 17·5°/0° (Gustavson, *l.c.*); vapour pressures (Kahlbaum, Zeitsch. physikal. Chem. 26, 626). At 240°–250° it is converted mainly into propylene dibromide, traces of propyl and *iso*propyl bromides, and of tribromopropanes also being formed (Faworsky and Sokownin, Annalen, 354, 325). It yields trimethylene by the action of zinc dust and acetic acid (Zelinsky and Schlesinger, Ber. 1908, 41, 2429), or of zinc and alcohol (von Wolkow and Menschutkin, J. Russ. Phys. Chem. Soc. 30, 559; Ber. 1898, 31, 3070; Berthelot, Compt. rend. 129, 483; Gustavson, J. pr. Chem. [ii.] 36, 300). By heating with 12 parts of water at 170° propaldehyde, acetone, and trimethylene glycol are produced; with less water part of the propaldehyde is converted into methylethylacraldehyde, whilst with only 6 parts of water phorone and mesityl oxide are the products (Rix, Monatsh. 1904, 25, 267; *cf.* Niederist, *ibid.* 3, 838). By heating with silver oxide and water trimethylene glycol is formed (Beilstein and Wiegand, Ber. 1882, 15, 1497; *cf.* Fortinski, J. Russ. Phys. Chem. Soc. 1913, 45, 568); sodium at 220° yields trimethylene. Alcoholic potash gives allyl bromide and ethyl allyl ether, whilst alcoholic ammonia in the cold yields trimethylene diamine. Aluminium bromide converts it into propylene dibromide (Gustavson, J. pr. Chem. [ii.] 36, 303).

Acetone dibromide, *ββ-dibromopropane, dibromoacetal* $CH_3{\cdot}CBr_2{\cdot}CH_3$. Prepared by the action of phosphorus tribromide (Linnemann, Annalen, 138, 125) or of phosphorus bromochloride (Friedel and Ladenburg, Zeitsch. Chem. 1868, 48) on acetone; by treating *β*-bromopropylene with hydrobromic acid (Reboul, Ann. Chim. [v.] 14, 465); or similarly from allylene (Reboul, *l.c.*).

B.p. 114°–114·5° (740 mm.); sp.gr. 1·8149 at 0°/0°, 1·7825 at 20°/20°. Heated at 240°–250° it yields propylene dibromide and traces of trimethylene dibromide (Faworsky and Sokownin, Annalen, 354, 325). Alcoholic potash or potassium acetate gives hydrogen bromide and *β*-bromopropylene; water at 160° yields acetone; with zinc and acetic acid propane is the product (Linnemann, Annalen, 161, 67).

Higher brominated derivatives, *v.* Lespieau, Bull. Soc. chim. [iii.] 7, 260; Ann. Chim. [vii.] 11, 253; Mouneyrat, Compt. rend. 127, 274; Bull. Soc. chim. [iii.] 19, 805, 809; Gustavson, J. pr. Chem. [ii.] 46, 159; Reboul, Ann. Chim. [v.] 14, 476, 482; Berthelot and Luca Annalen, 101, 76; Wurtz, *ibid.* 104, 207; Tollens, *ibid.* 156, 168; Kronstein, Ber. 1891, 24, 4245; Oppenheim, Annalen, 132, 124; Pinner, *ibid.* 179, 60; Prins. D. R. P. 261689.

Chloro Derivatives.

Propyl chloride, *α-chloropropane*

$CH_3 \cdot CH_2 \cdot CH_2Cl$

On chlorinating propane the chief product is propyl chloride, small quantities of higher chlorinated compounds also being formed (Schorlemmer, Annalen, 150, 209; 152, 159). Prepared by the action of iodine monochloride or of mercuric chloride on propyl iodide (Linnemann, *ibid.* 161, 37); by the interaction of propyl alcohol and hydrochloric acid or phosphorus pentachloride (Pierre and Puchot, *ibid.* 163, 266); by passing nitrosyl chloride into a toluene solution of propylamine at −15° to −20° (Solonina, J. Russ. Phys. Chem. Soc. 30, 431); by the action of hydriodic acid on epichlorhydrin (Silva, Compt. rend. 93, 739).

B.p. 44° (744 mm.) (Brühl, Annalen, 200, 179); crit. temp. 230·0; crit. press. 45·2 atm. (Berthoud); sp.gr. 0·9156 at 0°, 0·8918 at 19·8°, 0·8915 at 39° (Pierre and Puchot, *l.c.*); *cf.* Linnemann, *l.c.*; Zander, Annalen, 214, 156; Schiff, *ibid.* 220, 98). By heating with iodine monochloride, carbon tetrachloride and perchlorethane are produced (Krafft and Merz, Ber. 1875, 8, 1296); with aluminium chloride, bromide or iodide propylene and hydrochloric acid are the products (Kerez, Annalen, 231, 306; Mouneyrat, Bull. Soc. chim. [iii.] 21, 616); with antimony pentachloride, propylene dichloride (Meyer and Müller, J. pr. Chem. [ii.] 46, 161); with bromine and iron wire, propylene dibromide (Herzfelder, Ber. 1893, 26, 1260); with ethylamine, ethyl propylamine and ethyl dipropylamine (Arena, Chem. Zentr. 1907, ii. 1396).

***iso*Propyl chloride,** *β-chloropropane*

$CH_3 \cdot CHCl \cdot CH_3$

Prepared by the interaction of *iso*propyl iodide and mercuric chloride, or of propylene dichloride and hydriodic acid (Linnemann, Annalen, 136, 41); by passing nitrosyl chloride into a toluene solution of *iso*propylamine at −15° to −20° (Solonina, J. Russ. Phys. Chem. Soc. 30, 431).

B.p. 36·5°; sp.gr. 0·8588 at 20° (Zander, Annalen, 214, 157); 35·74° (corr.) (Thorpe). Chlorine in the sunlight yields acetone dichloride and a trace of propylene dichloride, whilst iodine monochloride (Friedel and Silva, Zeitsch. Chem. 1871, 489) or antimony pentachloride (Meyer and Müller, J. pr. Chem. [ii.] 46, 161; Silva, Compt. rend. 93, 739) give propylene dichloride. Heated with hydriodic acid, *iso*propyl iodide is produced; with bromine and iron wire, propylene dibromide (Herzfelder, Ber. 1893, 26, 1260); with ammonia, mono-, and di*iso*propylamines (Malbot, Bull. Soc. chim. [iii.] 4, 340, 632).

Propylidene dichloride, *αα-dichloropropane* $CH_3 \cdot CH_2 \cdot CHCl_2$. Prepared by the action of phosphorus pentachloride on propaldehyde (Reboul, Ann. Chim. [v.] 14, 458); b.p. 85°–87°; sp.gr. 1·143 at 10°. Alcoholic potassium hydroxide converts it into γ-chloropropylene, whilst antimony pentachloride yields *ααβ*-trichloropropane (Herzfelder, Ber. 1893, 26, 2434).

Propylene dichloride, *αβ-dichloropropane* $CH_3 \cdot CHCl \cdot CH_2Cl$. Prepared by the action of chlorine on propylene (Cahours, Annalen, 76, 283; Reynolds, *ibid.* 77, 124); by heating propyl or *iso*propyl chloride with antimony pentachloride (Meyer and Müller, J. pr. Chem. [ii.] 46, 176); by the action of chlorine on propyl chloride in the presence of aluminium chloride (Mouneyrat, Bull. Soc. Chim. [ii.] 21, 618); by heating allyl chloride and hydrochloric acid (Reboul, J. 1873, 321), or *iso*propyl chloride and chlorine (Friedel and Silva, Bull. Soc. chim, [ii.] 16, 3), in the latter case acetone dichloride also being formed.

B.p. 97·5°–98·5° (760·3 mm.) (Schiff, Ber. 1886, 19, 563); sp.gr. 1·1656 at 14°/14° (Linnemann, Annalen, 161, 62). Sodium amalgam or zinc and acetic acid are without action on propylene dichloride. Antimony pentachloride yields *ααβ*-trichloropropane, whilst chlorine in the presence of aluminium chloride gives *ααβ*- and *αββ*-trichloropropanes. Ten parts of hydriodic acid at 150° yield *iso*propyl chloride; twenty parts of water at 210°–220°, acetone and propaldehyde; lead oxide and water at 150°, propylene glycols; alcoholic potash, γ-chloropropylene together with a little β-chloropropylene.

Trimethylene dichloride, *αγ-dichloropropane* $CH_2Cl \cdot CH_2 \cdot CH_2Cl$. Prepared by chlorinating trimethylene (Gustavson, J. pr. Chem. [ii.] 50, 380); by heating trimethylene dibromide with mercuric chloride (Reboul, Ann. Chim. [v.] 14, 460), trimethylene diiodide with water and silver chloride (Herzfelder, Ber. 1893, 26, 2434), or trimethylene glycol with fuming hydrochloric acid (Freund, Monatsh. 2, 638).

B.p. 125°; sp.gr. 1·1896 at 17·6°/4°. Alcoholic potassium hydroxide converts it into allyl chloride, whilst antimony pentachloride at 120° yields *ααγ*-trichloropropane.

Acetone dichloride, *ββ-dichloropropane, dichloroacetol* $CH_3 \cdot CCl_2 \cdot CH_3$. Prepared by the interaction of acetone and phosphorus pentachloride (Friedel, Annalen, 112, 236); of allylene and fuming hydrochloric acid (Reboul, Zeitsch. Chem. 1871, 704; J. 1873, 321); together with propylene dichloride by the action of chlorine on *iso*propyl chloride (Friedel and Silva, Zeitsch. Chem. 1871, 489; *cf.* Friedel and Ladenburg, Annalen, 142, 315).

B.p. 69·7° (corr.); sp.gr. 1·827 at 16° (Linnemann, *ibid.* 161, 67). With a deficit of alcoholic potassium hydroxide, hydrochloric acid and β-chloropropylene are produced, whilst with an excess, allylene is formed. Sodium at 130°–150° yields propylene (Friedel and Ladenburg, Zeitsch. Chem. 1868, 48). By the action of 8 vols. of water at 160°–180° or of hydrochloric acid at 130°, acetone is produced. Antimony pentachloride yields *αββ*-trichloropropane (Herzfelder, Ber. 1893, 26, 1259).

Higher chlorinated derivatives: *v.* Friedel, Bull. Soc. chim. [ii.] 34, 129; Friedel and Silva, Zeitsch. Chem. 1871, 535, 682; Romburgh, Bull. Soc. chim. [ii.] 37, 103; Oppenheim, Annalen, 133, 383; Berthelot, *ibid.* 155, 108; Spring and Lecreiner, Bull. Soc. chim. [ii.] 48, 625; Borsche and Fittig, Annalen, 133, 114; Fittig and Pfeiffer, *ibid.* 135, 360; Hartenstein, J. pr. Chem. [ii.] 7, 313; Cahours, Annalen, 76, 283; Krafft and Merz, Ber. 1875, 8, 1296; Herzfelder, *ibid.* 1893, 26, 1258, 2435; Mouneyrat, Bull. Soc. chim. [iii.] 21, 619; Gustavson, J. pr. Chem. [ii.] 50, 381; Szenic and Taggesell, Ber. 1895, 28, 2667; Fritsch, Annalen, 297, 314; Prins. D. R. P. 261689; J. pr. Chem. 1914, [ii.]

89, 414–425; Böeseken, Van der Scheer, Rec. trav. chim. 1915, 34, 78.

For methods of formation of the propylene chlorohydrins, *see* Lennart Smith, Zeitsch. physikal. Chem. 1918, 93, 59.

Iodo Derivatives.

Propyl iodide, *α-iodopropane* $CH_3 \cdot CH_2 \cdot CH_2I$. Prepared by the action of iodine and red phosphorus on propyl alcohol (Chancel, Bull. Soc. chim. [ii.] 39, 648; *cf.* Linnemann, Annalen, 160, 240); b.p. 102·5°; sp.gr. 1·7829 at 20°/4° (Brühl, *ibid.* 203, 15; Dobriner, *ibid.* 243, 25; *cf.* Brown, Proc. Roy. Soc. 26, 238; Zander, Annalen, 214, 161; 102·23°, Thorpe and Rodger, Phil. Trans. 1894, A, ii. 467). With aluminium iodide it yields propane, whilst with aluminium chloride or bromide propylene is the product (Kerez, Annalen, 231, 306).

iso-**Propyl iodide,** *β-iodopropane* $CH_3 \cdot CHI \cdot CH_3$. Prepared by the action of hydriodic acid on propylene glycol (Würtz, Annalen, Suppl. 1, 381), glycerol (Erlenmeyer, Annalen, 126, 305; 139, 211; Markownikow, *ibid.* 138, 364), allyl iodide (Simpson, *ibid.* 129, 127), or *αβ*-propylene chloroiodide (Silva, Compt. rend. 93, 739; Sorokin, Zeitsch. Chem. 1870, 519); by the interaction of propylene and hydrogen iodide (Berthelot, Annalen, 104, 184; Erlenmeyer, *ibid.* 139, 228).

B.p. 89·5° (corr.); 89·7° (Thorpe and Rodger); sp.gr. 1·7109 at 15°/15° (Linnemann, *l.c.*; Brühl, *l.c.*); 1·7440 at 0°/0° (Brown, *l.c.*; Zander, *l.c.*). By heating in a sealed tube with water hydriodic acid and *iso*propyl alcohol are the products; with ammonia, mono*iso*propylamine; and with triethylamine, propylene and triethylammonium iodide (Reboul, Compt. rend. 93, 69; H. and A. Malbot, Bull. Soc. chim. [iii.] 4, 340, 632, 634). By interaction with magnesium, magnesium *iso*propyl iodide, propane, and propylene are formed (Tschelinzeff, J. Russ. Phys. Chem. Soc. 1904, 36, 549).

Propylene diiodide, *αβ-diiodopropane*

$CH_3 \cdot CHI \cdot CH_2I$

By the interaction of propylene and iodine (Berthelot and Luca, J. 1854, 453), or of allyl iodide and hydriodic acid (Malbot, Ann. Chim. [vi.] 19, 354); decomposes on distillation into hydrogen iodide and propylene. Sp.gr. 2·490 at 18·5°/18·5°; alcoholic potassium hydroxide converts it into propylene and iodine, whilst hydriodic acid yields *iso*propyl iodide.

Trimethylene diiodide, *αγ-diiodopropane*

$CH_2I \cdot CH_2 \cdot CH_2I$

Prepared by the interaction of trimethylene glycol and fuming hydriodic acid at 100° (Freund, Monatsh. 2, 640), or of trimethylene dibromide and potassium iodide in alcoholic solution (Perkin, Chem. Soc. Trans. 1887, 13; Henry, Ber. 1885, 18, 519); b.p. 227° (decomp.), 168°–170°/170 mm.; sp.gr. 2·59617 at 4°/4°, 2·57612 at 15°/15°, 2·56144 at 25°/25°. With mercuric nitrite it yields *αγ*-dinitropropane (Keppler and Meyer, *ibid.* 1892, 25, 1709).

Acetone diiodide, *ββ-diiodopropane, diiodoacetol* $CH_3 \cdot CI_2 \cdot CH_3$. Prepared by the action of concentrated hydriodic acid on allylene (Oppenheim, Zeitsch. Chem. 1865, 719; Semenow, *ibid.* 725); b.p. 147°–148° (decomp.); sp.gr. 2·15° at 0° (Oppenheim), 2·4458° at 0° (Semenow). Volatile in steam; with alcoholic potassium hydroxide it yields hydriodic acid and *β*-iodopropylene, whilst silver oxide yields acetone (Sorokin, *ibid.* 1871, 264).

Hydroxy Derivatives.

Propyl alcohol, *α-hydroxypropane*

$CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$

occurs in fusel oil from grain, potatoes, and beetroot (*v.* Fusel Oil). Formed in small quantities by the fermentation of glycerol by *Bacillus butylicus* (Fitz, Ber. 1880, 13, 1311; Morin, Bull. Soc. chim. 1887, [ii.] 48, 803). Prepared by heating allyl alcohol with potassium hydroxide (Tollens, Zeitsch. Chem. 1870, 457; 1871, 249); by reducing propaldehyde (Rossi, Annalen, 159, 80), or propionic anhydride (Linnemann, *ibid.* 148, 251; 160, 231; 161, 18) with sodium amalgam, or allyl alcohol with aluminium in 25 p.c. potassium hydroxide solution (Speranski, J. Russ. Phys. Chem. Soc. 1899, 31, 423); by the interaction of trioxymethylene and zinc ethyl and adding water to the product (Tischtschenko, *ibid.* 1887, 19, 483).

Colourless liquid; b.p. 96·6° (corr.) (Thorpe and Rodger); b.p. 97·19° (corr.) (Young and Fortey, Chem. Soc. Trans. 1902, 735; Brunel, Crenshaw and Tobin, J. Amer. Chem. Soc. 1921, 43, 561), 16·2°/10·22 mm., 22·3°/16·78 mm., 31·4°/30·2 mm., 35·6°/39·6 mm., 43·2°/62·18 mm. (Kahlbaum, Ber. 1883, 16, 2480; *cf.* Richardson, Chem. Soc. Trans. 1886, 763; Konowalow, Pogg. Ann. [ii.] 14, 41); sp.gr. 0·81923 at 0°/4° (Young and Fortey, *l.c.*), 0·80804 at 15° (Doroschewsky and Roschdestvensky, J. Russ. Phys. Chem. Soc. 1909, 41, 1428; *cf.* Zander, Annalen, 224, 79; Brühl, *ibid.* 203, 268; R. Schiff, *ibid.* 220, 101); for table of sp.gr. of aqueous solutions, *v.* Doroschewsky and Roschdestvensky, *l.c.*; heat of combustion (Zoubow, J. Russ. Phys. Chem. Soc. 1898, 30, 926); dielectric constant (Philip, Zeitsch. physikal. Chem. 1897, 24, 18; Abegg and Seitz, *ibid.* 23, 309; Jahn, *ibid.* 1892, 10, 316; Eykmann, Rec. trav. chim. 1893, 12, 277); electric conductivity (Doroschewsky and Roschdestvensky, *l.c.*); absorption spectrum (Spring. Rec. trav. chim. 1897, 16, 1). Miscible with water in all proportions; on shaking repeatedly with calcium chloride and distilling the product, a crystalline compound $CaCl_2, C_3H_7OH$ remains (Göttig, Ber. 1890, 23, 181). For solubilities of alkali haloids in propyl alcohol, *see* Turner and Bissett, Chem. Soc. Trans. 1913, 1904. Forms propoxides by replacement of the hydroxylic hydrogen by a metallic radicle. Oxidation with nitric acid yields carbon dioxide, oxalic acid, and propyl acetate (Klimenko, Ber. 1868, 1, 1604), whilst *Bacterium Aceti* (Brown), *B. Pasteurianum*, and *B. Kützingianum* yield propionic acid (Brown, Chem. Soc. Trans. 1886, 177; Seifert, Centr. Bakt. Par. 1897, 3, 337, 385). For products of oxidation obtained by passing vapour of propyl alcohol and air over a heated copper spiral, *v.* Orloff, J. Russ. Phys. Chem. Soc. 1908, 40, 203. By distillation with zinc, propylene and water are produced (Jahn, Ber. 1880, 13, 988); by slowly dropping propyl alcohol on to strongly heated zinc chloride, propylene, propaldehyde, and other products are formed (Le Bel and

Greene, Amer. Chem. J. 1880, 2, 23). Chlorine in the cold yields α-chloropropaldehyde, *as*-dichloropropyl ether, and other products (Brochet, Compt. rend. 1895, 121, 648; *cf.* Oddo and Cusmano, Gazz. chim. ital. 1905, 31, i. 46), whilst bromine gives dibromopropaldehyde. Potassium hydroxide and iodine yield iodoform (Lieben, Annalen, Suppl. 7, 230), whilst with bromine propylbromal is the product. Methyl iodide and propyl alcohol at 218° yield *n*-propyl ether (Wolkow, J. Russ. Phys. Chem. Soc. 1889, 21, 338).

***iso*Propyl alcohol**, *β-hydroxypropane*

$CH_3 \cdot CH(OH)CH_3$

occurs in fusel oil (*q.v.*). Prepared by reducing aqueous acetone (Friedel, Annalen, 124, 327; Linnemann, *ibid.* 136, 38); or by electrolysis (D. R. P. 113719, 1899); or by passing a mixture of acetone vapour and hydrogen over nickel heated to 115°–125°; or propylene oxide (Linnemann, *ibid.* 140, 178) with sodium amalgam; or by aluminium and sodium hydroxide in the cold; by heating *iso*propyl iodide with water (Niederist, *ibid.* 186, 391), or better with the addition of lead hydroxide (Flawitzky, *ibid.* 175, 380); by the interaction of zinc methyl and β-iodoethyl alcohol (Butlerow and Ossokin, *ibid.* 145, 257); together with propyl alcohol by the action of nitrous acid on *iso*propylamine (Linnemann, *ibid.* 161, 43; *cf.* Ber. 1877, 10, 1111; Meyer, *ibid.* 1876, 9, 535).

Colourless liquid; b.p. 82·9° corr.) (Thorpe and Rodger), 82·26° (Brunel Crenshaw and Tobin); 82·44° (corr.) (Young and Fortey, Chem. Soc. Trans. 1902, 735; Doroschewsky and Poljansky, J. Russ. Phys. Chem. Soc. 1910, 42, 1448; *cf.* Thorpe, Chem. Soc. Trans. 1897, 920); sp.gr. 0·80120 at 0°/4° (Young and Fortey, *l.c.*), 0·7982 at 4°/4°, 0·7903 at 15°/15° (Thorpe, *l.c.*; Louguinine, Ann. Chim. [vii.] 13, 289); for table of sp.gr. of aqueous solutions, *v.* Doroschewsky and Poljansky, *l.c.*; Lebo, J. Amer. Chem. Soc. 1921, 43, 1005; critical temperature 234·9° (Pawlewsky, Ber. 1882, 15, 3035); heat of combustion (Zoubow, J. Russ. Phys. Chem. Soc. 1898, 30, 926); dielectric constant (Loew, Ann. Physik. 66, 398; Drude, Zeitsch. physikal. Chem. 23, 39); absorption spectrum (Spring, Rec. trav. chim. 16, 1). Forms *iso*propoxides by replacement of the hydroxylic hydrogen by metallic radicles and yields a crystalline compound with calcium chloride. Chlorine converts *iso*propyl alcohol into *as*-tetrachloroacetone (Brochet, Ann. Chim. [vii.] 10, 124), whilst bromine yields *as*-tribromoacetone, acetone, and *iso*propyl bromide. Phosphorus trichloride yields di-*iso*propyl phosphite, *iso*propyl chloride, hydrogen chloride, and a small quantity of propylene (Milobdenski, J. Russ. Phys. Chem. Soc. 1898, 30, 730). Decomposes into propylene and water on heating with methyl iodide at 218° (Wolkow, *ibid.* 1889, 21, 337).

When oxidised by potassium permanganate in presence of potassium hydroxide yields carbon dioxide, oxalic acid, and acetic acid (Evans and Sefton, J. Amer. Chem. Soc. 1922, 44, 2271).

Propyleneglycol, *αβ-dihydroxypropane*

$CH_3 \cdot CH(OH)CH_2 \cdot OH$

Prepared by the interaction of powdered sodium hydroxide and glycerol, and subsequently distilling the product so formed (Morley and Green, Chem. Soc. Trans. 1885, 132); by reducing glycerol chlorhydrin with sodium amalgam (Lourenço, Annalen, 120, 91), or better by the action of acetyl bromide on glycerol, and reducing the compound thus formed with the zinc-copper couple and hydrochloric acid (Belohoubeck, Ber. 1881, 12, 1873); by heating 1 part of propylene dibromide with 26 parts of water (Niederist, Annalen, 196, 359); together with acetone and propaldehyde by the interaction of propylene dichloride or dibromide and water with lead oxide (Eletekow, J. Russ. Phys. Chem. Soc. 1878, 10, 210) or potassium carbonate (Hartmann, J. pr. Chem. 1897, [ii.] 55, 438); together with other products by the interaction of propylene dibromide and silver acetate (Wurtz, Ann. Chim. [iii.] 16, 383), or of allyl alcohol and 10 p.c. hydrochloric acid (Solonina, J. Russ. Phys. Chem. Soc. 1887, 19, 311).

Colourless liquid, having a sweet taste; b.p. 188°–189°; sp.gr. 1·051 at 0°, 1·0403 at 19·4° (Zander, Annalen, 214, 177); miscible with water or alcohol, soluble in 12–13 vols. ether. Oxidised by platinum black to lactic acid; by nitric acid to glycollic and oxalic acids; by chromic acid to acetic acid (Flawitzky, Ber. 1878, 11, 1256). An alkaline solution of permanganate gives carbonic acetic and oxalic acids (Evans and Witzemann, J. Amer. Chem. Soc. 1912, 34, 1086). Dilute sulphuric acid at 170° gives acetone, propaldehyde, and methylethylacraldehyde (Rix, Monatsh. 1904, 25, 267). Zinc chloride or dilute hydrochloric acid yield propaldehyde (Flawitzky, J. Russ. Phys. Chem. Soc. 1878, 10, 348; Linnemann, Annalen, 192, 61), whilst concentrated hydriodic acid yields *iso*propyl iodide. Either *sorbose bacterium* or *Mycoderma aceti* yields acetol (Kling, Compt. rend. 1901, 133, 231; 1899, 129, 1252; Bull. Soc. chim. 1901, [iii.] 25, 905), whilst *Bacterium termo* converts it into *l*-propylene glycol (Le Bel, J. 1881, 512). Bromine water yields acetol (Kling, Compt. rend. 1899, 129, 219; 128, 244). Sulphur chloride converts propylene glycol mainly into the chlorhydrin $CH_3 \cdot CH(OH)CH_2Cl$, although small quantities of the isomeric compound $CH_3 \cdot CHCl \cdot CH_2OH$ are probably also formed (Morley and Green, *l.c.*).

Trimethyleneglycol, *αγ-dihydroxypropane* n-*propylene glycol*, $CH_2OH \cdot CH_2 \cdot CH_2OH$, is a by-product in the manufacture of soap-lye glycerin, and is formed by the fermentation of the bone fat (*v.* GLYCERIN; and Noyes and Watkins, J. Amer. Chem. Soc. 1895, 17, 890; Freund, Monatsh. 1881, 2, 638; Rojahn, Zeitsch. anal. Chem. 1920, 58, 433; Cocks and Salway, J. Soc. Chem. Ind. 1922, 41, 18 T). It is present in considerable amount in the 'sweet water,' concentrates obtained by the fermentation of sugar to glycerol by the method of Connstein and Lüdecke. Formed by the fermentation of glycerol by *Schizomycetes* in the presence of calcium carbonate (Freund, Monatsh. 1881, 2, 638). Prepared by heating trimethylene dibromide (i.) with water (Niederist, *ibid.* 1882, 3, 839); (ii.) with water and silver oxide (Beilstein and Wiegand, Ber. 1882, 15, 1497); (iii.) with potassium hydroxide (Zander, Annalen, 214, 178); or (iv.) with sodium acetate, and subsequently hydrolysing the diacetate thus produced with barium hydroxide (Reboul, Ann. Chim.

1878, [v.] 14, 491). According to Henry (Chem. Zentr. 1899, i. 968) the hydrolysis is best effected with powdered potassium hydroxide under reduced pressure. Colourless liquid; b.p. 210°; sp.gr. 1·0573 $\frac{15°}{15°}$; miscible with water. By heating with sodium amalgam in amyl alcohol the monosodium derivative is formed, and on further treatment with metallic sodium this yields the disodium derivative (Parone, Boll, Chim. Farm. 1905, 44, 481).

For other derivatives, *see* Schmidt and Wilkendorff (Ber. 1919, 52 [B] 389); Rojahn (Ber. 1921, 54 [B] 3115).

For the preparation of optically active propylene glycol, *v.* Abderhalden and Eichwald (Ber. 1918, 51, 1312); Grün (Ber. 1919, 52, [B] 260).

Propyl cyanide, *butyronitrile*

$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CN$

Prepared by the interaction of ammonium butyrate and phosphorus pentoxide (Dumas, Annalen, 1847, 64, 334), or of acetonitrile, sodium, and ethyl iodide (Holtzwart, J. pr. Chem. 1889, [ii.] 39, 233); b.p. 116·3°–117°/750 mm.; sp.gr. 0·796 at 15° (van Erp. Rec. trav. chim. 1895, 14, 15). Reacts with sodium forming dimolecular propyl cyanide (iminobutyl propyl cyanide) (Wache, J. pr. Chem. 1889, [ii.] 39, 245). When administered to dogs it passes into the urine as ammonium thiocyanate (Lang, Arch. exp. Path. Pharm. 34, 247).

*iso***Propyl cyanide,** iso*butyronitrile*

$CH_3{\cdot}CH(CN)CH_3$

Prepared by the interaction of *iso*propyl iodide and potassium cyanide (Markowinkow, Zeitsch. Chem. 1865, 107), or together with *iso*butyramide by the action of potassium thiocyanate on *iso*butyric acid (Letts, Ber. 1872, 5, 669); b.p. 107°–108°. By the action of sodium two bases, $C_{12}H_{22}N_2$ and $C_{19}H_{34}N_6$, are produced (Meyer, J. pr. Chem. 1888, [ii.] 37, 400).

Propyl *iso***cyanide,** *propyl carbylamine*

$CH_3{\cdot}CH_2.CH_2{\cdot}NC$

Prepared by the interaction of propyl iodide and silver cyanide; b.p. 97°–99° (Wade, Chem. Soc. Proc. 1900, 157).

*iso***Propyl** *iso***cyanide,** iso*propyl carbylamine* $CH_3{\cdot}CH(NC)CH_3$. Prepared by the interaction of *iso*propyl iodide and silver cyanide; b.p. 87°; sp.gr. 0·759 at 0° (Gautier, Ann. Chim. 1869, [iv.] 17, 249). Dilute hydrochloric acid converts it into *iso*propylformamide.

*iso***Propyl** *iso***cyanate,** iso*propyl carbimide* $CH_3{\cdot}CH(NCO)CH_3$. Prepared by the interaction of *iso*propyl bromide and silver cyanate, or by heating bromo-*iso*butyramide with dry sodium hydroxide; b.p. 67° (Hofmann, Ber. 1882, 15, 756).

Propyl thiocyanate $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}SCN$. Prepared by the action of potassium thiocyanate on propyl bromide in alcoholic solution; b.p. 163° (Schmidt, Zeitsch. Chem. 1870, 576).

*iso***Propyl thiocyanate** $CH_3{\cdot}CH(SCN)CH_3$. Prepared by the action of potassium thiocyanate on *iso*propyl iodide in alcoholic solution; b.p. 149°/151°; sp.gr. 0·963 at 20° (Henry, Ber. 1869, 2, 496; *cf.* Gerlich, Annalen, 178, 83; Ber. 1885, 8, 650).

Propyl *iso***thiocyanate,** *propyl thiocarbimide, propyl mustard oil* $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}NCS$. Prepared by the interaction of propylamine and carbon disulphide and subsequent treatment with mercuric chloride, followed by distillation in steam; b.p. 152·7°/743 mm.; sp.gr. 0·9909 at 0° (Hecht, Ber. 1890, 23, 282).

*iso***Propyl** *iso***thiocyanate,** iso*propyl thiocarbimide,* iso*propyl mustard oil*

$CH_3.CH(NCS)CH_3$

Prepared similarly to the propyl compound (*v. supra*); b.p. 137°–137·5° (Jahn, Monatsh. 1882, 3, 168).

Propyl mercaptan $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}SH$. Prepared by the action of alcoholic potassium hydrosulphide on propyl bromide; b.p. 67°–68° (Roemer, Ber. 1873, 6, 784; Schatzmann, Annalen, 261, 7). Forms a mercury derivative $Hg(C_3H_7S)_2$, crystallising in plates, m.p. 68°.

*iso***Propyl mercaptan** $CH_3{\cdot}CH(SH)CH_3$. Prepared by the action of alcoholic potassium hydrosulphide on *iso*propyl iodide; b.p. 57°–60° (Claus. Ber. 1872, 5, 659; 1875, 8, 532). Forms a mercury derivative crystallising in plates. On oxidation with nitric acid the mercaptan yields *iso*propyl sulphonic acid.

Trimethylene sulphide $CH_2{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}S$, obtained from $\alpha\gamma$-dibromopropane and sodium sulphide, is a colourless highly mobile liquid with an unpleasant, penetrating odour, b.p. 93·8–94·2°/752 mm., D_4^{23} 1·0284, n_D^{23} 1·5059. With mercuric chloride forms a white microcrystalline compound C_3H_6S,H_9Cl_2. When oxidised by permanganate yields *trimethylene sulphone* $CH_2{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}SO_2$, needles, m.p. 75–76° (Grischkevitsch-Trochimovski, J. Russ. Phys. Chem. Soc. 1916, 48, 880).

Propyl sulphide $(CH_3{\cdot}CH_2{\cdot}CH_2)_2S$. Present in crude petroleum (Mabery and Smith, Amer. Chem. J. 1891, 13, 233; Ber. 1889, 22, 3303). Prepared by heating propyl chloride or iodide with alcoholic potassium sulphide; b.p. 141·5°–142·5°/772 mm. (Winssinger, Bull. Soc. chim. 1882, [ii.] 48, 190); sp.gr. 0·814 at 17° (Cahours, Compt. rend. 1873, 76, 133). Oxidised by nitric acid to propyl sulphoxide $(C_3H_7)_2SO_2$, which on treatment with potassium permanganate yields propyl sulphone, m.p. 29°–30° (Winssinger, *l.c.*). For compounds with platinum salts, *v.* Blomstrand, J. pr. Chem. 1888, [ii.] 38, 354, 498; Rudelius, *ibid.* 497, 508.

*iso***Propyl sulphide** $\left(\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH\right)_2S$. Prepared by heating *iso*propyl iodide with alcoholic potassium sulphide; b.p. 120·5°/763·1 mm. (Beckmann, *ibid.* 1878, [ii.] 17, 459). Oxidised by nitric acid to *iso*propyl sulphonic acid or by potassium permanganate to *iso*propyl sulphone, m.p. 36°. For compounds with platinum salts, *v.* Blomstrand, *l.c.*; Rudelius, *l.c.*

Propyl chlorosulphinate $Cl{\cdot}SO_2C_3H_7$, a colourless liquid, b.p. 78°/75 mm., obtained by adding thionyl chloride to well-cooled propyl alcohol. Decomposed by water into sulphur dioxide, hydrogen chloride and propyl alcohol (Stähler and Schirm, Ber. 1911, 44, 319).

Propyl sulphuric acid, *propyl hydrogen sulphate* $(C_3H_7)HSO_4$. Prepared by the action of sulphuric acid on propyl alcohol (Chancel, Compt. rend. 1853, 37, 410); an oil.

Propyl sulphate $(C_3H_7)_2SO_4$. Prepared by the action of chlorosulphonic acid on propyl alcohol (Mazurowska, J. pr. Chem. 1876, [ii.] 13, 162).

*iso***Propyl sulphuric acid** $(C_3H_7)HSO_4$. Prepared by the action of sulphuric acid on *iso*propyl alcohol or by the action of concentrated sulphuric acid on cardole (Spiegel, Chem. Zeit. 1895, 19, 1423); an oil.

Propyl nitrite $C_3H_7NO_2$. Prepared by heating propyl alcohol with amyl nitrite (Bertoni and Truffi, Gazz. chim. ital. 1884, 14, 23), or by passing nitrous fumes into propyl alcohol (Cahours, Compt. rend. 1873, 77, 745); b.p. 45°–46°; sp.gr. 0·935 at 21° (Cahours, *l.c.*); b.p. 57° (Bertoni and Truffi, *l.c.*); sp.gr. 0·9881 at 0° (Přibram and Handl, Monatsh. 1881, 2, 655); mol. ref. (Brühl, Zeitsch. physikal. Chem. 1897, 16, 214).

*iso***Propyl nitrite** $C_3H_7NO_2$. Prepared by the action of silver nitrite on *iso*propyl iodide (Bevad, J. Russ. Phys. Chem. Soc. 1892, 24, 125; Silva, Bull. Soc. chim. 1869, [ii.] 12, 227); b.p. 39°–39·5°/752 mm. (Bevad, *l.c.*); b.p. 45°; sp.gr. 0·856 at 0°, 0·844 at 25° (Silva, *l.c.*). By passing hydrogen chloride into a cold ethereal solution, *iso*nitrosochloracetone and ammonium chloride are produced (Kiesel, J. Russ. Phys. Chem. Soc. 1895, 27, 119).

Propyl nitrate $C_3H_7NO_3$. Prepared by heating propyl alcohol with nitric acid in the presence of a small quantity of urea (Wallach and Schulze, Ber. 1881, 14, 421); b.p. 110·5°; sp.gr. 1·0747 at 5°, 1·0631 at 15°, 1·0531 at 25° (Perkin, Chem. Soc. Trans. 1889, 683); mol. ref. (Lowenherz, Ber. 1890, 23, 2181; Brühl, Zeitsch. physikal. Chem. 1895, 16, 214).

*iso***Propyl nitrate** $C_3H_7NO_3$. Prepared by heating silver nitrate with *iso*propyl iodide; b.p. 101°–102°; sp.gr. 1·054 at 0°, 1·036 at 19° (Silva, Annalen, 1870, 154, 246).

Amines.

Propylamines. By the action of aqueous ammonia on propyl chloride (equal mols.) at 100°–110° for 10 hours, a mixture of monopropylamine (45 parts), dipropylamine (35 parts), and tripropylamine (20 parts) is obtained. These are separated by fractional distillation and purified as follows:—

(i.) To the *monopropylamine* ethyl oxalate is added with the formation of dipropyloxamide; (ii.) to the *dipropylamine* oxalic acid is added, dipropyloxamic acid being produced; (iii.) to the *tripropylamine* picric acid is added with the formation of the picrate (Chancel, Bull. Soc. chim. 1892, [iii.] 7, 405; *cf.* Malbot, Compt. rend. 1887, 104, 998; Vincent, *ibid.* 103, 208).

Propylamine, *α-aminopropane*

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$$

Prepared as above, or by the reduction of ethyl cyanide with zinc and hydrochloric acid (Mendius, Annalen, 121, 133; Siersch, *ibid.* 144, 137; Silva, Zeitsch. Chem. 1869, 638; Linnemann, Annalen, 161, 44); by the action of bromine followed by potassium hydroxide on butyramide (Hofmann, Ber. 1882, 15, 769); by heating 10 parts of propyl nitrate with 19 parts of alcoholic ammonia at 100° (Wallach and Schulze, Ber. 1881, 14, 422); by fusing glycine ethyl ester with sodium hydroxide (Curtius and Gobel, J. pr. Chem. 1888, [ii.] 37, 163). B.p. 49°; sp.gr. 0·7330 at 4°, 0·7222 at 15°, 0·7144 at 25° (Perkin, Chem. Soc. Trans. 1889, 693); crit. temp. 218°, crit. press. 50 atmos. (Vincent and Chappuis, Compt. rend. 1886, 103, 379); crit. temp. 223·8°; crit. press. 46·8 atmos. (Berthoud); elect. cond. (Oswald, J. pr. Chem. 1886, [ii.] 33, 361; Bredig, Zeitsch. physikal. Chem. 1894, 13, 295); mol. ref. (Brühl, *ibid.* 1895, 16, 214; Eykman, Rec. trav. chim. 1891, 12, 274). Forms a hydrate and compounds with many metallic chlorides (Matthews, J. Amer. Chem. Soc. 1898, 20, 829; Skraup and Wiegmann, Monatsh. 1889, 10, 112; Hjostdahl, J. 1882, 476). The *platinichloride* has m.p. 214°; the *picrate*, m.p. 135° (Chancel, *l.c.*). Chromic acid oxidises propylamine to propionic acid (Chapman and Thorpe, Annalen, 142, 176); hydrogen peroxide yields at low temperatures a white crystalline peroxide (Kurovski and Nisenmann, J. Russ. Phys. Chem. Soc. 1911, 43, 654). Nitrous acid yields propyl and *iso*propyl alcohols and propylene (Meyer and Forster, Ber. 1876, 9, 535); nitrosyl chloride gives nitrosodipropylamine and dipropylamine hydrochloride (Solonina, J. Russ. Phys. Chem. Soc. 1898, 30, 431, 449).

For other derivatives, *v.* Gabriel and Ohle (Ber. 1917, 50, 804); Jacobs, Heidelberger and Rolf (J. Amer. Chem. Soc. 1919, 41, 458); Abderhalden and Eichwald (Ber. 1918, 51, 1312).

Dipropylamine $(C_3H_7)_2NH$. For preparation, *v. supra*; b.p. 109·4°–110·4°; sp.gr. 0·7524 at 4°, 0·7430 at 15°, 0·7357 at 25° (Perkin, Chem. Soc. Trans. 1889, 693); elect. cond. (Bredig, *l.c.*). Forms a hydrate which is a liquid, sparingly soluble in water. The *picrate* has m.p. 75° (Chancel, *l.c.*).

Tripropylamine $(C_3H_7)_3N$. For preparation, *v. supra*; b.p. 156·5°; sp.gr. 0·7563 at 18·2° (Roemer, Ber. 1873, 6, 1101); elect. cond. (Bredig, *l.c.*). Forms a hydrate which is a liquid, very sparingly soluble in water.

Tetrapropylammonium iodide $(C_3H_7)_4NI$. Prepared by the interaction of concentrated ammonia and propyl iodide at 150° (Malbot, *l.c.*; *cf.* Roemer, Ber. 1873, 6, 784); prismatic needles, somewhat soluble in water, more readily so in alcohol, but less so in ether. Silver hydroxide yields *tetrapropylammonium hydroxide* as a deliquescent mass (Roemer, *l.c.*).

*iso*Propylamines. *iso*Propyl iodide and an equivalent quantity of strong aqueous ammonia react very slowly at the ordinary temperature, but the product consists entirely of mono*iso*propylamine hydriodide. At higher temperatures the action is quicker, but di*iso*propylamine hydriodide, propylene, and ammonium iodide are also produced (H. and A. Malbot, Compt. rend. 1890, 111, 650; *cf.* Jahn, Monatsh. 1882, 3, 166). According to Zande (Rec. trav. chim. 1889, 8, 205) by heating 40 grms. of alcoholic ammonia (15 p. c. NH_3) with 40 grms. of *iso*propyl iodide at 100° for 4½ hours, a mixture of mono- and di*iso*propylamine is obtained. The product is heated with a further quantity of *iso*-propyl iodide for ½ hour at 100°, and the di*iso*propylamine separated by conversion into the nitroso derivative. By the action of hydrochloric acid on *iso*propyl *iso*cyanide a mixture of the mono- and di*iso*propylamines is also obtained (Siersch, Annalen, 148, 263; *cf.* Gautier, Ann. Chim. [iv.] 17, 251).

*iso***Propylamine** $(CH_3)_2CH{\cdot}NH_2$. Prepared as above, or by the action of bromine followed by potassium hydroxide on *iso*butyramide (Hofmann, Ber. 1882, 15, 768); by reducing an alcoholic solution of acetonephenylhydrazone (Tafel, *ibid.* 1886, 19, 1926), acetoxime (Goldschmidt, *ibid.* 1887, 20, 728) or dihydroxyacetoxime (Piloty and Ruff, *ibid.* 1897, 30, 1664) with sodium amalgam. B.p. 33°–34° (Menschutkin, J. Russ. Phys. Chem. Soc. 1897, 29, 453); sp.gr. 0·690 at 18°; mol. ref. (Brühl, Zeitsch. physikal. Chem. 1895, 16, 214); elect. cond. (Bredig, *ibid.* 1894, 13, 295). Nitrous acid converts *iso*propylamine into *iso*propyl alcohol (Siersch, *l.c.*; Meyer and Forster, Ber. 1876, 9, 535); nitrosyl chloride yields nitrosodi*iso*propylamine and di*iso*propylamine hydrochloride (Solonina, J. Russ. Phys. Chem. Soc. 1898, 30, 431, 449). Forms compounds with metallic chlorides; the hydrochloride has m.p. 153°–155° (Skraup and Wiegmann, Monatsh. 1889, 10, 112).

Di*iso*propylamine $(C_3H_7)_2NH$. For preparation, *v. supra*; b.p. 83·5°–84°/743 mm.; sp.gr. 0·722 at 22°. The nitroso derivative

$$(C_3H_7)_2N(NO)$$

has m.p. 40°.

Diamines.

Propylene diamine, *αβ-diaminopropane*

$$CH_3{\cdot}CH(NH_2)CH_2{\cdot}NH_2$$

Prepared by heating propylene dibromide and alcoholic ammonia at 100° (Hofmann, Ber. 1873, 6, 308); a strongly alkaline liquid, b.p. 119°–120°. The hydrochloride $C_3H_{10}N_2,2HCl$ has m.p. 220°. Propylene diamine forms compounds with numerous metallic salts (Werner, Zeitsch. anorg. Chem. 1899, 21, 200). *l*-Propylene diamine has been prepared by the resolution of the *dl*- base with *d*-tartaric acid; it has b.p. 121°; sp.gr. 0·8612° at 23°/4°; $[\alpha]_D$ −29·65° (Tschugaeff and Sokoloff, Ber. 1909, 42, 55; 1907, 40, 3461; *cf.* Baumann, *ibid.* 1895, 28, 1180).

Trimethylene diamine, *αγ-diaminopropane* $CH_2(NH_2)CH_2{\cdot}CH_2{\cdot}NH_2$. Prepared by the interaction of trimethylene dibromide (1 part) and saturated alcoholic ammonia (8–9 parts) (Fischer and Koch, Ber. 1884, 17, 1799; Annalen, 1886, 232, 222; *cf.* Lellmann and Würthner, *ibid.* 1885, 228, 227); by the action of strong hydrochloric acid on trimethylene diphthalimide (Gabriel and Weiner, Ber. 1888, 21, 2670); by reducing *αγ*-dinitropropane with sodium amalgam and acetic acid (Keppler and Meyer, *ibid.* 1892, 25, 2638); b.p. 135°–136°/738 mm.; miscible with alcohol, ether, chloroform, or benzene. The hydrochloride $C_3H_{10}N_2,2HCl$ crystallises in large plates; on treatment with silver nitrite and water the hydrochloride yields allyl alcohol and other compounds (Demjanow, J. Russ. Phys. Chem. Soc. 1893, 25, 577).

Propylene $CH_3{\cdot}CH:CH_2$. Formed by passing the vapours or fusel oil (Reynolds, Annalen, 77, 118), petroleum (b.p. 60°–90°) (Prunier, J. 1873, 347), trimethylene (Tanatar, Ber. 1899, 32, 702, 1965), or other organic compounds through a red-hot tube; by distilling allyl iodide (Oppenheim, Annalen, Suppl. 6, 354). Best prepared by heating propyl alcohol with phosphorus pentoxide (Beilstein and Wiegand, Ber. 1882, 15, 1498) or by heating propyl or *iso*propyl alcohol with glacial phosphoric acid (Newth, Chem. Soc. Trans. 1901, 917). Propylene may be prepared in good yield by passing propyl alcohol over aluminium oxide or fragments of graphite crucibles at 360°, preferably under diminished pressure. It is purified by passing through a receiver cooled in ice, then over calcium chloride and potassium hydroxide, through a vessel cooled in a mixture of toluene and solid carbon dioxide and finally over calcium chloride (Trautz and Winkler, J. pr. Chem. 1922, 104, 44). Also prepared by heating propyl alcohol (4 vols.) with sulphuric acid (3 vols.) and 5 p.c. of anhydrous aluminium sulphate at 100°–110° (Senderens, Compt. rend. 1910, 151, 392); by heating *iso*propyl alcohol with fused zinc chloride (Friedel and Silva, J. 1873, 322); by the interaction of alcoholic potassium hydroxide with propyl iodide (Freund, Monatsh. 1882, 3, 633), or *iso*propyl iodide (Erlenmeyer, Annalen, 139, 228); by distilling glycerol with twice its weight of zinc-dust (Claus, Ber. 1885, 18, 2931); by heating allyl iodide with zinc and sulphuric acid or with mercury and hydrochloric acid (Berthelot and Luca, Annalen, 92, 309); by distilling allyl iodide (Linnemann, *ibid.* 161, 54; Gladstone and Tribe, Ber. 1873, 6, 1550; Niederist, Annalen, 196, 358), or allyl bromide (Wolkow and B. N. Menschutkin, J. Russ. Phys. Chem. Soc. 1898, 31, 3071) with zinc-dust in alcoholic solution; by the interaction of acetone dichloride (Friedel and Ladenburg, Zeitsch. Chem. 1868, 48) or acetone dibromide (Reboul, Ann. Chim. 1878, [v.]. 14, 488) with sodium at 130°–150°; by the action of zinc ethyl on perchloromethane (Beilstein and Rieth, Annalen, 124, 242), bromoform (Beilstein and Alexejew, J. 1864, 470), or dichloroacetal (Paterno, Annalen, 159, 134); by fusing a mixture of calcium oxalate and potassium acetate (Dusart, *ibid.* 97, 127); by heating thymol with phosphorus pentoxide (Engelhardt and Latschinow, Zeitsch. Chem. 1869, 616). By passing a mixture of acetylene and methane over heated (100°–200°) contact substances consisting of mixtures of noble metals (platinum, iridium, and palladium) and common metals (iron, nickel, copper, &c.) deposited electrolytically or by chemical reduction on a porous material, *e.g.* pumice (Heinemann, D. R. P. 315747, Chem. Zentr. 1920, 1920, ii. 186).

Colourless gas, which can be liquefied under a pressure of 7–8 atmos. (Moltschanoffsky, J. Russ. Phys. Chem. Soc. 1889, 21, 32) or under atmospheric pressure by immersing in liquid air; sp.gr. of liquid 0·647; b.p. −47·8° (Burrell and Robertson); −47·0° (Maas and Wright); m.p. −182·5°; −47·8° at 750 mm. (Trautz and Winkler, J. pr. Chem. 1922, 104, 44); crit. temp. 92·1°; crit. pressure 45·34 atmos. Heat of combustion (const. press.) 499·3 Cal. (Berthelot and Matignon, Bull. Soc. chim. 1894, [ii.] 11, 739). One vol. of water at $t°$ dissolves $0{\cdot}446506 - 0{\cdot}022075t + 0{\cdot}0005388^2$ vol. propylene (Than, Annalen, 123, 187); absolute alcohol dissolves 12–13 vols. One grm. of pure sulphuric acid absorbs 470 c.c. of propylene, forming the compound $[(CH_3)_2CH]_2SO_4$, which on distillation with water yields *iso*propyl alcohol (Berthelot, Ann. Chim. 1895, [vii.] 4, 104). According to Plant and Sidgwick (J. Soc. Chem. Ind.

1921, 40, 14) propylene is far more readily absorbed than ethylene in sulphuric acid, and the reactions are more complex. In addition to propyl hydrogen sulphate and propyl sulphate, a colourless oil separates, which does not contain sulphur and appears to consist of saturated compounds. It reacts with sodium, and is probably a mixture of open-chain secondary alcohols. Oxidation with potassium permangamate or with chromic acid yields carbon dioxide and formic, acetic, and oxalic acids (O. and F. Zeidler, Annalen, 197, 249). For the action of propylene on sulphur monochloride, *v.* Coffey (Chem. Soc. Trans. 1921, 119, 94).

Trimethylene, cyclo*propane,* cyclo*trimethylene* $CH_2<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$. Prepared by the action of sodium (Freund, Monatsh. 1882, 3, 626; *cf.* Reboul, Ann. Chim. 1878, [v.] 14, 488) or zinc (Gustavson, J. pr. Chem. 1887, [ii.] 36, 300; Trautz and Winkler, J. pr. Chem. 1922, 104, 37) on trimethylene dibromide in alcoholic solution. According to Wolkow and B. N. Mentschutkin (Ber. 1898, 31, 3067) and Tanatar (*ibid.* 1899, 32, 702, 1965) the gas obtained by Gustavson's method always contains propylene; by passing the gas through bromine the propylene is absorbed and the trimethylene is obtained in a pure state. It has been shown, however, that the presence of propylene in the gas is due to the fact that trimethylene dibromide usually contains some propylene dibromide, and that if the trimethylene dibromide is quite pure, no propylene is obtained. If the first portion of the gas obtained by this method is rejected, the remainder is pure trimethylene (Gustavson, J. pr. Chem. 1907, [ii.] 76, 512; 1899, [ii.] 59, 302; Willstätter and Bruce, Ber. 1907, 40, 4456). Amyl alcohol may be substituted for ethyl alcohol in this preparation (Haehn, Arch. Pharm. 1907, 245, 518; Partheil, Verh. deut. Naturforsch. Aerzte, 1907, ii. 159).

Colourless gas, which can be liquefied under a pressure of 5–6 atmos. (Moltschanoffsky, J. Russ. Phys. Chem. Soc. 1889, 21, 32), or under atmospheric pressure by immersing in liquid air; sp.gr. of liquid 0·720; it has also been solidified, m.p. −126°; (−127°, Trautz and Winkler); b.p. −35° (*circa*) (Ladenburg and Krügel, Ber. 1899, 32, 1821), −34·5° at 750 mm. (Trautz and Winkler). Heat of combustion (const. press.) 507·8 Cal. (Berthelot and Matignon, Bull. Soc. chim. 1894, [iii.] 11, 739). Trimethylene, when exposed, to a red heat remains unchanged, but at higher temperatures decomposes into ethylene, hydrogen, paraffins, and other products; by passing through a red-hot tube it is converted into propylene, but if air is present formaldehyde is produced (Tanatar, Ber. 1896, 29, 1297; and *l.c.*; Wolkow and B. N. Mentschutkin, *l.c.*; Berthelot, Compt. rend. 1899, 129, 483). At 100° in the presence of platinum black propylene is produced (Tanatar, Zeitsch. physikal. Chem. 1902, 41, 735), whilst with nickel reduction to propane is effected (Willstätter and Bruce, *l.c.*). One grm. of pure sulphuric acid absorbs 480 c.c. of trimethylene, yielding the compound $(CH_3{\cdot}CH_2{\cdot}CH_2)_2SO_4$, which on distillation with water gives propyl alcohol (Berthelot, Ann. Chim. 1895, [vii.] 4, 102). Chlorine reacts explosively in the sunlight, but in diffused daylight yields dichlorotrimethylene, trimethylene dichloride, β-chloropropylidine dichloride, and trichlorhydrin (Gustavson, J. pr. Chem. 1894, [ii.] 50, 381; 1890, [ii.] 42, 495). By the action of bromine trimethylene dibromide together with some propylene dibromide is formed; dry bromine acts very slowly, but if hydrogen bromide be present, the latter acts as a catalyst, greatly accelerating the reaction (Gustavson, *ibid.* 1899, [ii.] 59, 302; Compt. rend. 1900, 131, 233).

PROPYL ACETIC ACID *v.* Valeric acids.

PROPYLBENZENE *v.* Cumenes.

iso-**PROPYLSUCCINIC ACID** *v.* Pimelic acid.

PROTACTINIUM, Pa. at.wt. 230 ? A radioactive element, held by Hahn and Meitner (Phys. Zeits. 20, 1919, 127) to be the parent of actinium. The new element, a higher homologue of tantalum, emits α-rays of 3·14 cm. range, and its half-value period lies between 1200 and 180,000 years (*see* also Ber. 1919, 52, 1812).

PROTALBIC ACID. A substance prepared by Paal (Ber. 1902, 35, 2195) by heating egg albumin at 100° with a 3 p.c. solution of sodium hydroxide and adding acetic acid. After purification by dialysis and washing with alcohol forms a white powder, soluble in acids and alkalis and in acetone. An alkaline solution treated with platinic chloride and a slight excess of hydrazine hydrate gives a colloidal form of platinum. Black lustrous scales, readily soluble in water giving a dark brown opalescent solution, stable, and active as a catalyst.

PROTAN. Tannin nucleo proteid.

PROTARGOL *v.* Synthetic drugs.

PROTEINS. The chief nitrogenous constituents of both plants and animals are complex substances, forming a group to which at various times different names have been applied, such as albumens, albumenoids, and proteins (Ger. *Eiweiss-stoffe,* after a typical member of the group, egg-white). The class name now generally adopted is 'protein,' the terms 'albumen' and 'albuminoids' being employed to designate certain sub-groups. Altogether more than fifty proteins are known to occur naturally in plants and animals, which differ from one another in physical and chemical properties. It is only comparatively recently that any definite knowledge as to their chemical constitution has been attained, and owing to the labours of Emil Fischer and his pupils, who have devised a systematic method of chemical examination, a fairly clear view is now obtainable of the way in which their highly complex molecules are built up. On hydrolysis they yield a large number of amino acids, for which E. Fischer has devised a method of approximately quantitative estimation, and the individual proteins differ from one another in the number and quantities of these acids obtainable from them by acid hydrolysis. The proteins are therefore essentially 'polypeptides,' which are formed by the conjugation of a large number of amino-acids, according to the scheme—

$$\begin{matrix}R & & R' & & & & R''' & & R^n\\ | & & | & & & & | & & |\\ (COOH{-}CH{-}NH){-}(CO{-}CH{-}NH) & & & & & & {-}(CO{-}CH{-}NH){-}CO & \ldots & NH{-}(CO{-}CH{-}NH_2)\end{matrix}$$

The following are the amino acids which have, up to the present, been isolated as hydrolysis products of the proteins :—

A. Monoamino carboxylic acids.

1. Glycine $C_2H_5NO_2$, or aminoacetic acid
$CH_2(NH_2)COOH$

2. Alanine $C_3H_7NO_2$, or α-aminopropionic acid
$CH_3{\cdot}CH(NH_2)COOH$

3. Valine $C_5H_{11}NO_2$, or α-amino*iso*valeric acid
$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH{\cdot}CH(NH_2)COOH$

4. Leucine $C_6H_{13}NO_2$, or α-amino-γ-methyl valeric acid
$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH{\cdot}CH_2{\cdot}CH(NH_2)COOH$

5. *iso*Leucine $C_6H_{13}NO_2$, or α-amino-β-methyl valeric acid
$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!CH{\cdot}CH(NH_2)COOH$

6. Phenylalanine $C_9H_{11}NO_2$, or β-phenyl-α-aminopropionic acid
$C_6H_5{\cdot}CH_2{\cdot}CH(NH_2)COOH$

7. Tyrosine $C_9H_{11}NO_3$, or β-parahydroxyphenyl-α-aminopropionic acid
$(OH)C_6H_4{\cdot}CH_2{\cdot}CH(NH_2)COOH$

8. Serine $C_3H_7NO_2$, or β-hydroxy-α-aminopropionic acid
$CH_2(OH)CH(NH_2)COOH$

9. Cystine $C_6H_{12}N_2O_4S_2$, or β-disulphido-α-aminopropionic acid
$COOH{\cdot}CH(NH_2CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}CH(NH_2)COOH$

B. Monoamino dicarboxylic acids.

10. Aspartic acid $C_4H_7NO_4$, or aminosuccinic acid
$COOH{\cdot}CH_2{\cdot}CH(NH_2)COOH$

11. Glutamic acid $C_5H_9NO_4$, or α-aminoglutaric acid
$COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2)COOH$

12 β-Hydroxyglutamic acid
$COOH{\cdot}CH(NH_2)CH(OH){\cdot}CH_2{\cdot}COOH$

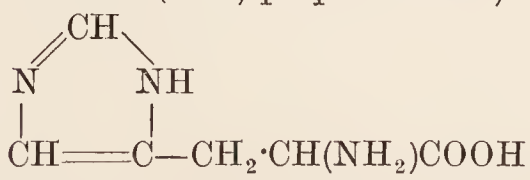
C. Diaminomonocarboxylic acids.

13. Arginine $C_6H_{14}N_4O_2$, or α-amino-δ-guanino-*n*-valeric acid
$HN{=}C\!<\!\begin{matrix}NH_2\\NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2CH(NH_2)COOH\end{matrix}$

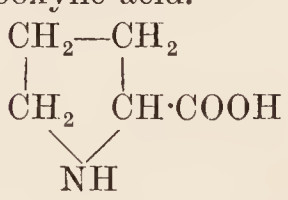
14. Lysine $C_6H_{14}N_2O_2$, or $\alpha\epsilon$-diaminohexoic acid
$(NH_2)CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2)COOH$

D. Heterocyclic compounds.

15. Histidine $C_6H_9N_3O_2$, or β-iminazole-α-aminopropionic acid (α-amino-β-glyoxaline-4(or 5)-propionic acid).

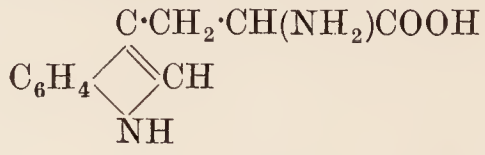


16. Proline $C_5H_9NO_2$, or pyrrolidine-2-carboxylic acid.



17. Oxyproline $C_5H_9NO_3$, or hydroxypyrrolidine-2-carboxylic acid, a hydroxy derivative of the above.

18. Tryptophan $C_{11}H_{12}N_2O_2$, or β-indole-α-aminoproprionic acid



acid No. 12 has recently been described by Dakin (Bio-Chem. J. 1918, 12, 306).

Other acids are probably obtainable by the hydrolysis of proteins which have not yet been isolated. In few cases have more than 70 p.c. of the theoretically obtainable amino acids been isolated from any given protein. Generally the yield is appreciably smaller. This is partly due to the imperfect methods of isolation of acids from the complex mixture which is formed in the hydrolysis, but partly probably also to the fact that other amino acids are obtainable, which have not yet been isolated in a pure state.

The quantitative estimation of the hydrolysis products.—The method of isolating in an approximately quantitative manner the mono-amino acids derived from proteins is due chiefly to Emil Fischer. The protein is boiled with either sulphuric or hydrochloric acid ; as a rule, three times the weight of the latter acid of sp.gr. 1·19 is employed, and the heating is then continued until the biuret reaction (*see* below) has completely disappeared. The hydrolysis mixture is then concentrated *in vacuô* to a small volume, saturated with hydrochloric acid gas and allowed to stand for some days at 0°. The greater part of the glutamic acid then separates in the form of its hydrochloride. The filtrate from this substance is concentrated to syrup *in vacuô*, and the latter is then dissolved in absolute alcohol (3 litres for 1 kilo. of protein), and the alcoholic solution is saturated with hydrochloric acid gas. In this way the monoamino acids are esterified, but owing to the formation of water in the process, it does not proceed to completion at once. The alcohol is therefore distilled off *in vacuô*, and the residue is redissolved in alcohol, and the alcoholic solution is again treated with hydrochloric acid, and, after standing, concentrated. If glycine is present in any large quantity it separates at this stage in the form of the hydrochloride of its ester. The esterification is, if necessary, repeated a third time. The esters of the hydrochlorides of the amino acids are finally obtained in the form of a thick syrup, from which the free esters must be prepared. This operation requires great care and skill, owing to the ease with which these substances are hydrolysed. The syrup is dissolved in about an equal volume of water, the solution cooled with ice and salt, and covered with a layer of ether. 33 p.c. caustic soda is then added in small quantities at a time, alternately with solid potassium carbonate, and the mixture is vigorously shaken after each addition, so that the amino acid esters, as they are set free from their hydrochlorides, are dissolved by the ether. As much caustic soda must be added as to combine with the whole of the hydrochloric acid and as much carbonate as will form a pasty mass, and the ether must be continuously poured off from the mass and renewed. The ether is then distilled off after drying the solution over

anhydrous sodium sulphate, and the residual dark-coloured oil is subjected to fractional distilliation *in vacuô* to separate as completely as possible the amino acids from one another. Modifications of the process of preparing the free esters from their hydrochlorides have been suggested, such, for example, as the treatment of the alcoholic solutions of the hydrochloride with the theoretical quantity of sodium ethoxide.

Various modifications for preparing the esters of the amino-acids have been suggested. Levene and Van Slyke (J. Biol. Chem. 1909, 6, 391) decompose the hydrochlorides of the amino-esters by means of barium oxide. Forman (Bio-Chem. J. 1919, 13, 378) prepares the hydrochlorides of the esters in the following manner. After hydrolysis of the protein by hydrochloric acid, the greater part of the acid is removed by distillation, and the mixture is then treated first of all with freshly precipitated lead hydroxide, and then by litharge. The amino-acids are then obtained in the form of the lead salts, which are prepared in a dry form by evaporating off the water. These are suspended in alcohol, and a current of dry hydrochloric acid gas is passed in. After esterification, the excess of hydrochloric acid is removed, for the most part by evaporation, and the remainder by precipitation as ammonium chloride by a saturated alcoholic solution of ammonia. The hydrochlorides of the esters are then taken up (after evaporating off the alcohol) with chloroform, and decomposed in chloroform solution by the gradual addition of anhydrous baryta. The free esters are then distilled, first on a water-bath under a pressure of about 10 mm., such as can be produced by the ordinary laboratory water-pump, and afterwards under a pressure of 0·5 mm., which can be produced by a double Geryk pump worked by a motor; a liquid air trap is generally inserted between the pump and motor, to condense the volatile vapours. A good vacuum can also be produced by means of cocoa-nut charcoal cooled in liquid air. The following fractions are obtainable. Fraction I., b.p. under 40° at 10 mm. pressure; contains glycine and alanine. Fraction II., b.p. 40°–60° at 10 mm. pressure; contains alanine, leucine, and proline. Fraction III., b.p. 60°–90° at 10 mm. pressure; contains valine, leucine, and proline. Fraction IV., water-bath, 100° at 0·5 mm. pressure; contains leucine and proline. Fraction V., oil-bath, 100°–130° at 0·5 mm. pressure; contains phenylalanine, aspartic acid, glutamic acid and serine. Fraction VI., oil bath, 130°–160°, contains also phenylalanine, glutamic and aspartic acids and serine. This fractional distillation of esters gives, therefore, only a very incomplete separation of the various amino acids. To get more complete separation the various fractions of the esters are hydrolysed, the lower fractions by water and the higher ones by barium hydroxide solution. The free acids obtained from the various fractions are separated from one another by a somewhat complex process of fractional crystallisation. The separation is rendered especially difficult by the fact that the amino acids, as they exist in the original protein, are optically active, and undergo partial racemisation during the process of hydrolysis. There are therefore present, in addition to the different amino acids, mixture of optical isomerides of the same acid. For these reasons it will be readily understood that a strict quantitative estimation of the various hydrolysis products has so far not been possible. These remarks apply more especially to valine, leucine and *iso*leucine. Certain of the other esters and acids have, however, special properties, which greatly facilitate their isolation. Thus proline, for example, is the only acid which is readily soluble in alcohol; the ester of phenylalanine can be readily separated from the other esters of the fraction in which it is contained by adding water and extracting the mixture with ether, when phenylalanine ester will be the only one dissolved; serine ester can be obtained by adding a small quantity of water to the fraction which contains it, and then adding to the mixture light petroleum, which causes the serine ester alone to separate. For details as to the methods of separation of the esters reference should be made to special text-books and monographs (*see* below).

Certain monoamino acids cannot be obtained in the form of amino acid esters that can be fractionally distilled; included amongst these are the important substances tyrosine, cystine, and tryptophan.

Tyrosine and cystine can be estimated by hydrolysing the proteins completely with hydrochloric acid, distilling off the greater part of the excess *in vacuô*, and then neutralising the residue. The two slightly soluble amino acids then crystallise out, and can be separated (but not quite quantitatively) from one another by fractional crystallisation from dilute ammonia. A simpler method of preparing cystine from wool, which gives a large yield of this substance on hydrolysis, has been suggested by Folin (Journal of Biol. Chem. 1910, 8, 9). The protein (the keratins, hair, and horn yield the largest amount of cystine) is hydrolysed with hydrochloric acid, and the mixture is then treated with solid sodium acetate until it is no longer acid to congo-red. On standing, cystine separates. It is recrystallised from 3 to 5 p.c. hydrochloric acid solution. The mother-liquor from cystine yields tyrosine. Tryptophan is usually destroyed during acid hydrolysis, and is therefore generally prepared from hydrolysis products which have been obtained by digestion with the enzyme trypsin (*see* below). As soon as the digestion mixture gives a maximal coloration when acidified and treated with bromine (which colour is due to tryptophan), it is acidified, boiled, filtered, sulphuric acid is added till 5 p.c. is present in the mixture, and then mercuric sulphate. The tryptophan is thereby precipitated as a mercury salt.

The diamino acids or hexone bases.—These acids, arginine, lysine, and histidine, were, on account of their basic character, formerly known as the hexone bases, and, owing to the investigations of Kossel and Kutcher, fairly accurate methods exist for determining the amounts of these three substances, which are yielded by protein hydrolysis. The principle of the method of isolation consists in precipitating the bases from the acid solution of hydrolysis products by means of phosphotungstic acid, decomposing the phosphotungstates by baryta, and precipitating from the solution of free bases the arginine and histidine by silver sulphate and excess of barium hydroxide. From the filtrate

of the silver salts of these two bases, the third base, lysine, can be precipitated either as phosphotungstate or as picrate. Arginine and histidine can be separated from one another by decomposing the silver salts, and then reprecipitating them from neutral solution by means of silver nitrate and barium carbonate. The histidine only is thereby precipitated and is filtered off; the silver salt of the other substance can only be made to come down from the filtrate when the latter is made strongly alkaline with baryta. From the respective fractions of silver salts arginine and histidine can be prepared pure in the form of picrolonates. By estimating the nitrogen in aliquot portions of the various fractions, the amounts of arginine, histidine, and lysine can be quantitatively determined. For details of the method reference must be made to special text-books.

Another method for estimating the diamino acids obtainable from proteins by hydrolysis is due to van Slyke. It can be carried out when only small amounts of material are available, and appears to be a relatively simple analytical process (Ber. 1910, 33, 3170; J. Biol. Chem. 1911, 9, 186; 10, 16).

A new method of investigating the hydrolysis products of the proteins has recently been introduced by Dakin (Bio-Chem. J. 1918, 12, 290, and J. Biol. Chem. 1921, 44, 499). After hydrolysis with sulphuric acid, the latter is removed by baryta, and the concentrated solution of amino-acids is then extracted in a continuous extraction apparatus by means of butyl alcohol. The mono-amino-monocarboxylic acids are thereby extracted, and separate out directly in a crystalline form, whereas the diamino-acids and the dicarboxylic acids remain unextracted. During the course of these investigations, Dakin discovered an amino-acid, hitherto undescribed, viz. hydroxy-glutamic acid, to which reference has been made, and also certain keto-piperazides, which are possibly only artifacts, and not true hydrolysis products. The method by Dakin promises to be of some importance.

Another method by means of which the amino-acids can be obtained in crystalline form without employing the esterification process has been described by Buston and Schryver (Bio-Chem. J. 1921, 15, 636). The aqueous solution of the amino-acids, diluted with twice the bulk of alcohol, is treated alternately with baryta and carbon dioxide. The amino-acids are thereby precipitated in the form of carbamates, which can be obtained in fractions and afterwards decomposed by boiling with water, which causes a separation in barium carbonate and the free amino-acid.

It will be seen from the above accounts that the methods of quantitatively separating the amino acids from one another are complex, and in the case of the mono-amino acids, at any rate, only approximately accurate. Nevertheless, the main chemical distinction between the various proteins depends on the quantities of the different amino acids that they yield on hydrolysis. This statement is illustrated by the accompanying table, which gives the percentage yields of the hydrolysis products obtained from certain typical proteins.

—	Salmine	Globulin (horse blood)	Egg albumin	Serum albumin	Serum globulin	Edestin (hemp-seed)	Glutelin (wheat)	Gliadin (wheat)	Caseinogen (cow's milk)	Gelatin	Vitellin (egg)	Keratin (ox-horn)
Glycine . .	—	—	0	0	3·5	3·8	0·4	0·7	0	16·5	1·1	0·4
Alanine . .	—	4·19	2·1	2·7	2·2	3·6	0·3	2·7	0·9	0·8	+	1·2
Valine . .	4·3	—	—	—	+	+	—	0·4	1·0	1·0	2·4	5·7
Leucine . .	—	29·04	6·1	20·0	18·7	20·9	4·1	6·0	10·5	2·1	11·0	18·3
*iso*Leucine .	—	—	—	—	—	—	—	—	—	—	—	—
Phenylalanine.	—	4·24	4·4	3·1	3·8	2·4	1·0	2·6	3·2	0·4	2·8	3·0
Tyrosine .	—	1·33	1·1	2·1	2·5	2·1	1·9	2·4	4·5	0	1·6	4·6
Serine . .	7·8	0·56	—	0·6	—	0·4	—	0·2	0·23	0·4	—	0·7
Cystine . .	—	0·31	0·3	2·5	0·7	0·3	—	—	0·06	—	—	6·8
Proline . .	11·0	2·34	2·3	1·0	2·8	1·7	4·0	2·4	3·1	5·2	3·3	3·6
Hydroxyproline	—	1·04	—	—	—	2·0	—	—	0·25	3·0	—	—
Aspartic acid .	—	4·43	1·5	3·1	2·5	4·5	0·7	1·3	1·2	0·6	0·5	2·5
Glutamic acid .	—	1·73	8·0	7·7	8·5	6·3	24·0	31·5	11·0	0·9	12·2	3·0
Tryptophan .	—	+	+	+	+	+	+	1·0	1·5	0	—	—
Arginine .	7·4	5·42	—	—	—	11·7	4·4	2·8	4·84	7·6	—	2·3
Lysine . .	0	4·28	—	—	—	1·0	2·2	0·0	5·80	2·8	—	—
Histidine .	0	10·96	—	—	—	1·1	1·2	1·2	2·59	0·4	—	—
Ammonia .	—	—	—	—	—	—	2·5	4·1	1·6	0·4	—	—

Some more complete and accurate numbers for the hydrolysis product of certain proteins have been obtained recently. For those of casein, *see* Forman (Bio-Chem. J. 1919, 13, 391), and for those of gelatin (Dakin, Journ. Biol. Chem. 1921, 44, 499).

The numbers in the above table are due to various observers.

I. The Reactions of the Proteins.

The reactions which serve for the quantitative detection of the proteins may be divided into two classes, viz. precipitation reactions and colour reactions. The latter are due, for the most part, to individual amino acids, such as tryptophan, which can be obtained by hydrolysis of the proteins. As each amino acid is not contained in every protein, these colour reactions are not general.

Precipitation reactions.—I. On heating many

protein solutions, a precipitate or coagulum is formed, the process of production being known as coagulation. This phenomenon only takes place in the presence of water, and Chick and Martin (Journ. Physiol. 1910, 40, 404) have shown that it is due to a chemical reaction taking place between the protein and the water, and the rate of formation follows the ordinary laws of mass action. The temperature at which a coagulum forms was formerly regarded in the light of a physical constant, which could serve for the characterisation of individual proteins, in the same way that a melting-point can be used to characterise a simpler organic compound. In the course of the investigations just mentioned, however, it has been shown that a coagulum can be formed at different temperatures, but more rapidly at higher than at lower temperatures. The point of observed incipient coagulation will depend, therefore, on the rate at which the protein solution is heated. The observed coagulation point is also markedly affected by the physical and chemical character of the solution, especially the surface tension. It has been shown by Michaelis and Rona (Biochem. Zeitsch. 1910, 27, 38) that the optimum condition for the coagulation of a protein is when the protein and solution are isoelectric.[1] This happens, in the case of dialysed egg-albumin and other proteins, when a small amount of acid has been added to the solution. For this reason, coagulation is generally carried out in solutions which have been slightly acidified with acetic acid, or with acid sodium phosphate. Chick and Martin have shown that coagulation can be best carried out in solutions which have been made distinctly acid to litmus paper by butyric acid (J. Physiol. 1911, 431). The presence of salt and other dissolved substances, in that these alter the physical character of the solutions, will also affect the coagulation point of the proteins. The heat coagulation is, perhaps, one of the most characteristic properties of large classes of proteins, although it can no longer be regarded in the light of a physical constant. II. Proteins can be precipitated from solution by various mineral acids. Nitric acid is generally employed; when allowed to flow on to the surface of a protein solution, it forms a white ring (Heller's test). Metaphosphoric acid (but not the ortho- or pyro- acids) is also a good precipitant. III. Ferrocyanic acid (a mixture of potassium ferrocyanide and acetic acid) is a good precipitant. Some proteins are soluble in excess of the reagent. IV. The salts of heavy metals precipitate proteins from solution. This reaction is very complex, and does not follow the ordinary mass reaction laws. When small quantities of salts of heavy metals are added to the solutions, either chemical action (formation of metallic salt of a protein) or physical absorption can take place according to the conditions of experiment. In the presence of larger quantities ordinary salt precipitation of proteins (*see* below) can take place. V. Proteins are precipitated by the ordinary alkaloidal reagents; such as phosphotungstic and phosphomolybdic acids, potassium mercuric iodide, potassium bismuth iodide, picric acid, and tannic acid. The last-named is perhaps the most widely used precipitant, and is generally employed in the form of the so-called Almen's reagent (4 grms. tannic acid in 8 c.c. 25 p.c. acetic acid +190 c.c. 40–50 p.c. alcohol). VI. Trichloracetic and sulphosalicylic acid are good precipitants. VII. Uranyl acetate precipitates proteins.

Colour reactions.—I. Very dilute copper sulphate solution in the presence of sodium hydroxide and protein produces a reddish-violet to violet-blue coloration. This is generally known as the *biuret* reaction. II. On boiling proteins with nitric acid, yellow flakes or yellow solutions are formed, which on making alkaline become orange. This so-called *xantho-proteic* reaction is probably due to the presence of a benzene ring. III. By dissolving mercury in nitric acid without getting rid of the nitrous acid, the so-called *Millon's* reagent can be prepared. This solution gives with proteins a precipitate, which become pinkish on boiling. This reaction is due to the presence of tyrosine. IV. A large number of colour reactions are due to the presence of the tryptophan group and are in consequence not yielded by all proteins. The chief of these is the reaction of *Hopkins* and *Cole*, which is a modification of the earlier so-called *Adamkiewicz* reaction. A few drops of a solution of glyoxylic acid, prepared by reducing oxalic acid solution with sodium amalgam, are added to the protein solution, and then concentrated sulphuric acid is poured in; at the junction of the liquids a reddish-violet colour is produced in those proteins which contain a tryptophan group. Other reactions are Reichel's (blue colour with alcoholic solution of benzaldehyde, dilute sulphuric acid (1 : 1), and ferric chloride), and Rhode's (reddish to dark violet colour with dimethylaminobenzaldehyde and concentrated sulphuric acid). V. A series of reactions is given with several proteins, which is due to the presence of a carbohydrate group. In these cases it is not definitely proved whether the carbohydrate group is actually contained in the protein, or whether the latter is contaminated with a glyco-protein (*see* classification of proteins, below). The chief of these are the *Molisch-Udransky* reaction and *Bial's* orcin reaction. In the former, concentrated sulphuric acid is added to the protein solution containing a few drops of an alcoholic solution of α-naphthol; a violet colour is thereby produced which turns yellow on addition of sodium hydroxide or alcohol. Bial's reaction is carried out by the addition of dried protein to fuming hydrochloric acid; when solution has taken place after warming, a little solid orcinol and a drop of ferric chloride solution are added, and a green colour is produced. VI. On warming proteins containing sulphur with sodium hydroxide in the presence of a lead salt, a black coloration is produced showing the presence of cystine. VII. Diacetyl in the presence of potassium hydroxide solution gives a pink colour with proteins, accompanied sometimes with a fluorescence; the latter phenomenon disappears if

[1] It has been shown by Powis, however, that aggregation of colloids takes place, not when the colloid and dispersion medium are isoelectric, but when the difference of potential is diminished to a certain critical maximum (Zeitsch. Physikal. Chem. 1915, 89, 179). In view of his results, those of Michaelis and Rona require some revision.

the alkali be allowed to hydrolyse the protein before the addition of the diacetyl. The colour is due to the presence of a group—

$$NH:C(NH_2)NH\cdot R$$

(Harden and Norris, Journ. Physiol. 1911, 42, 332). VIII. Ruhemann has shown that triketohydrindene hydrate gives a blue colour with proteins, peptones and amino acids (Chem. Soc. Trans. 1910, 97, 2025). For conditions of reaction, *v.* Aberhalden and Schmidt, Zeitsch. Physiol. Chem. 1911, 79, 37.

II. The Chief Physical Properties of the Proteins.

Colloidal nature.—The most striking physical properties of the proteins may be attributed to their colloidal nature. Owing to the large size of the molecules of the majority of the proteins, they will not pass through animal and vegetable membranes, such as parchment paper, layers of collodin, 'sausage skin,' &c. They can consequently be readily separated from simpler substances by the process of dialysis. Owing to their ability to absorb simpler substances, however, the last traces of the latter can be removed only with very great difficulty, and it has often been questioned whether the inorganic ash yielded by proteins after prolonged dialysis is not due to inorganic substances in actual chemical combination with the protein. Another method, analogous to dialysis for separating proteins from simpler substances is that of filtration under pressure through gelatin and collodion membranes. The former are hardened in formaldehyde before use, and the latter can be prepared from solutions of collodion either in acetic acid or alcohol and ether. Filtration can take place under either high or low pressures. In the former case, a Berkfeld or other similar filtering candle is employed, which is impregnated with gelatin solution and then formalised. In the latter case, filter-papers are impregnated *in vacuô* with either gelatin or collodion; the stronger the solution employed, the greater the pressure ultimately required for filtration. A special apparatus has been devised for the method of filtration by Bechhold, who has designated the process by the name of 'ultrafiltration.' The simpler molecules pass the filters, whereas the proteins remain behind.

Proteins can be carried out from solution by other colloids, and upon this property methods have been founded for separating proteins from solution. For this purpose two solutions have up to the present been chiefly employed, viz. mastic dissolved in 50 p.c. alcohol and dialysed ferric hydroxide. If these colloidal solutions be mixed with solutions not too rich in proteins, and some salt solution, such as that of magnesium sulphate, be added, the two colloids are precipitated together. In these cases the reaction is not always reversible, in that the protein cannot always be dissolved out from the precipitate by water; it can, however, be conveniently employed for separating proteins from solutions where they interfere with other reactions. Proteins can also be removed from solution by solid substances which act as absorbents, such as precipitated silicic acid, meerschaum, and iron oxide; under favourable conditions, this removal is complete. Proteins also, by virtue of their colloidal properties, can 'protect' other colloids and prevent the latter from being precipitated from solution. This property is best demonstrated by means of colloidal gold solutions. If an electrolyte be added to the bright-red colloidal gold solution, produced by the reduction of gold chloride by formaldehyde, a precipitate of the non-colloidal gold is produced. Zsigmondy has shown that proteins can inhibit this precipitation, and that the different members of the class show considerable variations with regard to the amount required to reveal this effect. He therefore has proposed to regard the quantity of a protein just necessary to inhibit the precipitation of gold from a certain standard colloidal solution by a definite amount of electrolyte as a factor which shall serve for the identification of individual proteins. This factor he designates the 'gold number' (Zeitsch. anal. Chem. 1901, 40, 697).

The solubility of the proteins and the salting out from solutions.—The different proteins show great variations in the behaviour towards solvents. Some, such as keratin, horn, &c., are insoluble in all solvents; others, such as egg-albumin and serum albumin, are easily soluble (*i.e.* if not coagulated) in water, but insoluble in organic solvents. Other proteins, again, such as the globulins, are insoluble in pure water, but soluble in salt solutions when the latter are not too concentrated, and other proteins are soluble only in dilute acids or alkalis, such as the glutenins. All these kinds of proteins, are insoluble in organic solvents. In addition there is a class of proteins which are insoluble both in water and absolute alcohol, but soluble in dilute alcohol (and also acetone). Certain plant proteins, known as the gliadins, possess this property, and Osborne has obtained a similar protein from milk (Osborne and Wakeman, J. Biol. Chem. 1918, 33, 243). Aqueous solutions of proteins, furthermore, possess an important characteristic property. The majority of proteins can be precipitated from their aqueous solutions by the addition of salts. The precipitating power of salts varies greatly, and is an additive function, depending on both the acid and the base. Some salts will not precipitate at all, as the necessary concentration for precipitation is not attained when their saturation point is reached. The precipitation produced by salts is reversible, *i.e.* the precipitate redissolves on dilution of the solution. The proteins, furthermore, show great variation amongst themselves in the amount of salt necessary to precipitate them from solution. Thus, for example, the globulins are precipitated when their aqueous solutions are saturated by magnesium sulphate and half saturated with ammonium sulphate: the albumins, under these conditions, remain in solution. The method of salt precipitation of the proteins has been, therefore, extensively applied for the separation of proteins from solution, and from one another; in fact, it is the only general method which is available for the separation from one another of proteins which are soluble in water. It was employed by Denis as long ago as 1835, and but little progress has been made since the publication of Denis' monographs in 1856 and 1859 on the method of protein separation. The salts

most commonly employed for precipitation are ammonium sulphate, magnesium sulphate, zinc sulphate, and (less frequently) sodium chloride. Limits of concentration can be experimentally determined at which protein precipitate begins and ends, and these limits will vary with the different proteins, and also (but to a lesser degree) with the concentration of the protein solution. The method of separation of proteins from one another by fractional salt precipitation is, however, far from efficient. If a salt be added to a mixture of proteins, as soon as the limit of concentration is reached at which the more readily precipitated protein falls out, precipitation will commence. The precipitate will contain, however, not only the protein of which the salt concentration limit has been reached, but some also of the less readily precipitable protein. The only method available, therefore, for separating water soluble proteins from one another is an imperfect one, and this fact accounts for a great deal of the uncertainty as to the homogeneity of a large number of proteins which have been submitted to investigation.

Reference has been already made to the co-precipitation of proteins by other colloids.

Crystallisation of proteins.—A number of proteins are capable of existing in crystalline forms. The so-called aleurone grains found in plants and first observed by Hartwig in 1850 were subsequently shown to consist of proteins, and in 1877 Schmiedeberg succeeded in re-crystallising the aleurone grains of Brazil nuts. Since that date several proteins have been obtained in crystalline form. The chief of these are serum and egg-albumins, and certain plant globulins (*see* below), of which edestin is a type. The conjugated protein hæmoglobin can also be obtained in crystalline form. Egg and serum albumins are obtained in crystalline form by mixing solutions of egg and serum proteins with an equal bulk of concentrated ammonium sulphate, filtering off the precipitated globulins, and then acidifying the filtrate, acetic acid being generally employed for this purpose in the case of egg-albumin, and sulphuric acid in the case of serum albumin. The plant proteins, such as edestin, can be obtained in a crystalline form by allowing the protein to separate out slowly from a not too concentrated (not more than 8 p.c.) saline solution, which had been previously warmed to 60°. 5 p.c. sodium chloride solution is generally employed. Many methods have been suggested for the preparation of hæmoglobin crystals. One of the most commonly adopted methods is that of diluting a hæmoglobin solution with one-fourth its volume of alcohol and cooling the mixture to 0°, when crystals separate out. There is a considerable literature dealing with the crystallisation of proteins, and much discussion as to the nature of the crystals, which do not behave entirely like those of simpler substances. It is also not known whether the natural proteins undergo any kind of chemical change during the course of crystallisation. In the case of egg-albumin, it has been thought that the crystallised protein is a salt, and its 'gold number' (*see* above) differs very appreciably from that of the non-crystallised protein.

Other physical properties of the proteins.—Few of the other physical properties can be regarded as typical of individual proteins. Their solutions are optically active, being lævo-rotatory with the exception of hæmoglobin, which, according to Gamgee and Croft-Hill, is slightly dextro-rotatory ($[\alpha]_D = +10{\cdot}4°$). The number of reliable determinations is small; others contain considerable sources of error, for, as the molecular weight is large, very small quantities of either acid or alkali may convert the amphoteric substance into a salt, and thus cause large errors in determination of physical constants. For this reason, the majority of physical constants are of practically no value for the characterisation of individual proteins. Other physical constants which have been determined are molecular weight, estimated chiefly by the measurement of the osmotic pressure of a solution contained in a membrane permeable to crystalloids and in contact with water or an aqueous solution, and electrolytic conductivity, of which measurements have been made in the course of investigations dealing with the salt formation of proteins. Much work remains to be done with reference to osmotic pressure, which probably varies with the state of aggregation of the protein. It is advisable to repeat here, that the coagulation temperature of proteins cannot be regarded as a physical constant (*see* above).

III. Classification of the Proteins.

Not sufficient is known yet of the true chemical structure of the proteins to found a rational classification based upon differences of chemical constitution. The classification adopted is therefore more or less of an empirical nature, founded only to a small extent on chemical distinctions, but chiefly on crude differences in physical properties. A classification was provisionally adopted by a joint committee of the Chemical and Physiological Societies, and subsequently submitted to American physiologists and chemists, who adopted a very similar but somewhat more complete classification. The appended classification includes the additions contained in the American list which were not contained in the English suggestions.

A. The Simple Proteins.

(*a*) *The protamines.*—This class is a very limited one, the members of which are contained only in the testes of certain fish in conjunction with nucleic acid. These proteins are distinguished by their extremely basic character and high percentage of nitrogen (25–30 p.c.), and the large amount of diamino acids which they yield on hydrolysis (80 p.c. or more). They can be precipitated from basic solutions by phosphotungstic acid and other alkaloidal reagents.

(*b*) *The histones.*—The members of this class are less basic than the protamines, but more basic than the following class of the albumins. There is no hard-and-fast distinction between the three classes. Like the protamines, the histones are also for the most part found in combination with nucleic acid as nucleoproteins, which form the nucleus of the cells. The histones contain 17–20 p.c. nitrogen, and yield on hydrolysis more diamino acids than albumins, but less than the protamines. They can be

obtained from the nuclei of the blood-corpuscles of birds, from thymus glands, and from the ripe spermatozoa of various fish.

(*c*) *The albumins.*—This is a very widely distributed class of proteins, the members of which are soluble in water, forming solutions which coagulate on heating. The animal albumins are not precipitated from neutral solutions by saturation with sodium chloride and magnesium sulphate and half saturation with ammonium sulphate. In this way they are distinguished from the globulins. The albumins derived from plants include generally those proteins which are soluble in water, as distinguished from those soluble in saline solutions only. The solutions of plant proteins also coagulate on heating, but, in distinction to animal albumins, some of them are precipitated from aqueous solution by half-saturation with ammonium sulphate. Both the animal and vegetable albumins are generally substances of amphoteric reaction, being both weakly acid and weakly basic. They contain, as a rule, about 16 p.c. nitrogen.

(*d*) *The globulins.*—This class includes the proteins, which are generally insoluble in water, but soluble in saline solutions of moderate concentration. They are precipitated by saturation of their solutions with sodium chloride and magnesium sulphate, and by half-saturation with ammonium sulphate.

(*e*) *The prolamines.*—The members of this class were formerly called the gliadins. They are the vegetable proteins, which are insoluble in absolute alcohol or water, but soluble in diluted alcohol (70 p.c.). Osborne designates them as prolamines, as they yield on hydrolysis a relatively large amount of proline and ammonia.

(*f*) *The glutelins.*—These are the vegetable proteins, which are insoluble in dilute alcohol, water, and salt solutions. They can be dissolved by dilute acids and alkalis.

(*g*) *The scleroproteins.*—The proteins of this class were formerly called the *albuminoids.* Included in this class is a miscellaneous collection of proteins of various character, such as horn, hair, silk, gelatin, &c. They are derived, as the name indicates, chiefly from the connective and supporting tissues, and have no common distinguishing properties, which can serve to characterise them as a class. Gelatin is soluble in water, but other members of the class are soluble in no solvents.

B. The Conjugated Proteins.

The proteins of this class are found to contain groups which were formerly designated 'prosthetic groups,' which do not yield only amino acids on hydrolysis.

(*a*) *The nucleoproteins.*—Proteins found in combination with nucleic acid. These are said to form the chief constituent of nuclei, and are widely distributed.

(*b*) *The glycoproteins*, or proteins found in combination with a carbohydrate group.

(*c*) *The hæmoglobins*, or proteins found in combination with the chromatogenic substance hæmin. Hæmoglobins form the red pigment of blood of various animals. Certain pigments of the algæ are thought to be allied, as well as pigments derived from the bloods of invertebrates.

(*d*) *The phosphoproteins.*—These proteins readily yield phosphoric acid on gentle hydrolysis with alkali. Included in this class are caseinogen, the chief protein of milk, and vitellin from egg-yolk. It is not certain whether this class should be included amongst the conjugated proteins.

(*e*) *The lipoproteins.*—Very little is known with certainty as to this class. It cannot be stated definitely whether the fatty substances which are often isolated with proteins are in chemical combination or only physically adsorbed.

C. The Derived Proteins.

The substances included under this heading are derived from proteins by hydrolysis either by enzymes or by gentle treatment with acid and alkalis. They still give some of the definite protein reactions.

(*a*) *The proteans or metaproteins.*—This class includes those substances derived from natural proteins by gentle treatment with acids or alkalis at moderate temperatures (in the incubator). In the former case, 'acid albumins' are formed, which are precipitated from solution on neutralisation, giving a precipitate which redissolves on addition of excess of alkali; in the latter case 'alkali albumins' are formed, which are precipitated on neutralisation with acid, but dissolve on addition of excess. These represent, perhaps, the most complex of the hydrolysis degradation products of the proteins. In this class should be included, perhaps, the so-called 'racemised proteins' described by Dakin (J. Biol. Chem. 1912, 18, 357, and Dakin and Dudley, *ibid.* 1913, 15, 263 and 271), which are not attacked by proteoelastic ferments and pass through the alimentary tract of animals unchanged.

(*b*) *The coagulated proteins.*—The phenomena of coagulation have been already discussed.

(*c*) *The proteoses.*—These substances are derived from proteins by enzymatic digestion. The proteoses are still somewhat complex substances, and can be precipitated from solution by salts, for which purpose zinc sulphate and ammonium sulphate are generally employed. The proteoses give characteristic protein reactions, such as the biuret reaction, and are not coagulated on heating.

(*d*) *The peptones.*—These are still simpler hydrolytic degradation products of proteins, and differ from the proteoses in that they are not precipitated from solutions by salts, even on saturation.

(*e*) *The peptides.*—Under this designation are included still simpler hydrolytic degradation products of proteins than the peptones, substances, for example, which yield on hydrolysis two or three amino acids only. There is no hard-and-fast line of demarcation between this class and the classes containing the more complex substances, such as the peptones. The peptides are generally crystalline substances, whereas the peptones are not. Very few peptides have up to the present been isolated directly by hydrolysis of proteins (*see* E. Fischer and Abderhalden, Ber. 1906, 39, 752, 2315; 1907, 40, 3544; Osborne and Clapp, Amer. Journ. Physiol. 1907,

18, 123). A large number of peptides have, however, been obtained synthetically by E. Fischer and his pupils. The preparation of these products may be regarded as the first stage in protein synthesis.

In the appended table is given a list of the chief naturally occurring proteins, with their origin and the class to which they are assigned. By reference to the description of the various classes given above, a conception can in most cases be formed as to the method of isolation. Thus the albumens can be extracted from natural products by water, the globulins by not too concentrated salt solutions, the prolamines by alcohol, &c. Some of the proteins are insoluble in solvents, such as horn, silk, and other sclero-proteins. These can be prepared by separating the other constituents of the raw products by extraction with water, acids, ether, &c., when they alone will remain undissolved :—

THE CHIEF NATURAL PROTEINS.[1]

Vegetable Proteins.

Name	Origin	Class
Abrin	Abrus seeds	Albumin
Amandin	Almonds	Globulin
Avenalin	Oats	,,
Castanin	Chestnuts	,,
Conglutins	Different lupins	,,
Corylin	Hazel-nuts	,,
Edestin	Hemp-seed	,,
Excelsin	Brazil-nuts	,,
Globulin	Squash-seeds	,,
,,	Cotton seeds	,,
Gliadin	Wheat	Prolamine
Glutelin	,,	Glutelin
Glycinin	Soya-bean	Globulin
Hordein	Barley	Prolamine
Juglasin	Walnut	Globulin
Legumelin	Lentil, horse-bean, vetch, &c.	Albumin
Legumin	,, ,, ,,	Globulin, precipitated by $\frac{6}{10}$ saturation with ammonium sulphate
Leucosine	Wheat	Albumin
Maysin	Maize	Globulin
Oryzenin	Rice seeds	Glutelin
Phaseolin	Kidney-bean	Globulin
Phycocyan,[2] Phycoerythrin	Ceramium rubrum	Chromoproteins
Ricin	Castor bean	Albumin
Tuberin	Potato tuber	Globulin
Vicillin	Lentil, horse-bean, vetch, &c.	Globulin, precipitated by $\frac{7}{10}$ saturation with ammonium sulphate
Vignin	Cow-pea	Globulin
Zein	Maize	Prolamine

Animal Proteins.

Albumin of egg (ovalbumin)	Eggs	Albumin
Albumin of milk (lact-albumin)	Milk	,,
Albumin of serum	Serum	,,
Bence-Jones protein	Certain pathological urines	Globulin (?)
Caseinogen	Milk	Phosphoprotein
Chondroproteins	Cartilage, tendons, etc.	Glycoproteins
Clupeine	Testes of herring	Protamine
Collagen	Connective tissue	Scleroprotein
Conalbumin (?)	Eggs	Albumin
Conchiolin	Shell of lamellibranchs	Scleroprotein
Cornein	Coral	Scleroprotein
α- and β-Crystallins	Lens of eye	Globulins
Cyclopterine	Testes of cyclops	Protamine
Ealstin	Ligamentum nucæ	Scleroprotein
Fibrinogen. Yields fibrin on clotting	Blood	Globulin
Gadus histone	Testes of Gadus	Histone
Gelatin	Closely allied to collagen	Scleroprotein
Globin	Separated from chromo-protein of blood	Histone (?)
Globulin of egg (ovoglobulin)	Eggs	Globulin

[1] See, however, next paragraph.

[2] Kylin, Zeitsch. physiol. Chem. 1910, 69, 169.

Name	Origin	Class
Globulin of milk (lacto-globulin)	Milk	Globulin
,, serum	Serum	,,
Gorgonin	Skeletal tissue, Gorgonia cavollini	Scleroprotein
Hæmoglobin	Blood	Conjugated protein
Histone of thymus	Thymus gland	Histone
Keratins (various)	Hair, horn, nail, &c.	Scleroproteins
Lota histone	Testes of Lota	Histone
Myosin (para myosinogen)	Striated muscular tissue	Globulin
Myogen (myosinogen)	,, ,, ,,	Albumin
Mucins and mucoids	Various secreting glands (Animal mucilagenous substances generally)	Glycoproteins
Nucleoproteins	Animal and vegetable cells (supposed constituent of nucleus)	Nucleoproteins
Onuphin	Onuphis tubicola (worm)	Scleroprotein
Reticulin	Mucosa, small intestine of pig, &c.	,,
Salmine	Testes of salmon	Protamine
Scombrine	Testes of mackerel	,,
Silk gelatin	Silk	Scleroprotein
Silk fibroin	Silk	,,
Spongin	Sponges	,,
Sturine	Testes of sturgeon	Protamine
Thyreoglobulin	Thyroid gland	Globulin
Vitellin	Yolk of eggs	Phosphoprotein

IV. The Separation and Identification of the Natural Proteins.

One of the chief difficultics encountered in the investigation of the proteins is that due to their separation from one another. So great has this been that in very many of the cases it is impossible to state whether a substance described under a given name is a chemical entity or a mixture. In the case of insoluble substances, such as the keratins, this statement can be readily understood. But even in the case of the soluble proteins, no satisfactory method for complete separation exists. This is due to the colloidal nature of the substances, so that if one substance is separated from solution, it will carry down with it, in state of adsorption, other substances, which in its absence would remain in solution. For these reasons, and in particular that the identification of an individual protein is not altogether easy, the list of proteins given above must be regarded as tentative only. It includes, however, most of the proteins which have been described under various names.

Separation of Proteins from one another. A few proteins, especially some of vegetable origin, can be separated by taking advantage of the fact that they are soluble in dilute alcohol. Others are soluble only in saline solution, and many of the vegetable proteins, furthermore, can be recrystallised from such solutions. Even in this case, as Osborne has shown, the product obtained is not pure, but is a mixture of the protein and its salt. The usual method for separating from one another proteins which are soluble in watcr is that of fractional precipitation by salts. For evcry protein in a given concentration therc is a particular degree of saturation for cach precipitating salt, at which the protein commences to separate from solution, and a certain degree of saturation at which the precipitation is complete. This method, which has been already discussed (*see* p. 462), is, however, very imperfect, and it is probably impossible in most cases to obtain a complete separation of two soluble proteins. A crude separation of such substances as globulins from albumins can, however, be accomplished (*cf.* Wiener, Zeitsch. physiol. Chem. 1911, 74, 29).

The Identification of Proteins. The chief characteristic of individual proteins is the number and quantity of the various amino acids which are yielded on hydrolysis. A quantitative hydrolysis experiment is, however, only possible when relatively large amounts of material are available, and is an operation requiring a long time for its performance. It is therefore necessary in most cases to find some physical and chemical constants which may serve for identification.

A. *Physical constants.*—Such well-defined constants as boiling-point, melting-point, which are used for identifying simpler substances, are not found in the case of the proteins. The temperature of heat coagulation (p. 461) has been already discussed, and as mentioned above, cannot be regarded as a reliable constant. Neither can the optical rotation, although most proteins are optically active. This is due to the large molecular weight of the proteins, and also their amphoteric character, which allows them to form salts in most cases with acids or bases in solution. A small quantity of an acid or base can therefore convert a relatively large amount of protein into salt, and thus considerably alter the physical properties of its solution. As, furthermore, it is difficult to free entirely protein solutions from electrolytes, even after prolonged dialysis, it may be readily understood that few determinations of physical constants of proteins are reliable. The most reliable,

perhaps, as it is to a great extent independent of the factors just mentioned, is the precipitability by salts, and as has been suggested, the capacity for protecting colloidal gold from precipitation (' gold number ') (*see* p. 462). On the whole the chemical methods are the more trustworthy for identification.

B. *Chemical constants.*—The differences between the empirical compositions of the proteins are in the majority of cases small as regards the nitrogen, carbon, and hydrogen. In a few cases of the very basic proteins (the protamines) the total nitrogen is high. The chief difference is, however, in the sulphur constant, which is very readily determined by ordinary analytical methods. This factor gives a measure of the cystine in the molecule, and varies from 0 in certain proteins to 5 p.c. in human hair. The nucleoproteins contain phosphorus in the prosthetic group as nucleic acid, and the phosphoproteins yield phosphoric acid on hydrolysis at 37° with 1 p.c. sodium hydroxide. A few proteins contain halogens; the chief of these is the protein of the thyroid gland which contains iodine; this element is also contained in gorgonin, and iodine and bromine have also been isolated from several other scleroproteins derived from the supporting system of marine animals.

Another series of chemical constants which can be readily determined with small quantities of materials are the nitrogen distribution numbers, which are sometimes called the 'Haussmann numbers.' It will be remembered that the relative amounts of mono- amino and diamino acids vary very largely in the different proteins. The diamino acids are precipitated from the hydrolysis mixture by phosphotungstic acid. Proteins, furthermore, yield on hydrolysis small quantities of ammonia, which is supposed to be derived from nitrogen combined as 'amide,' and which can be readily estimated by making the hydrolysis mixture slightly alkaline (with magnesium hydroxide) and distilling off *in vacuô*. The distribution, therefore, of the total nitrogen of the protein between the 'amide' nitrogen, which can be distilled off as ammonia, the 'diamino acid' nitrogen, which is precipitated by phosphotungstic acid, and the 'mono- amino acid' nitrogen, which remains in the filtrate from this precipitate, is the chemical constant of proteins which is most readily determined and is most characteristic.

The phosphotungstic precipitate ('diamino'-fraction) contains the bases arginine, histidine, and lysine. Van Slyke has worked out a method by means of which each of these can be estimated. The bases are set free from the phosphotungstate precipitate by barium hydroxide. The total nitrogen can be estimated in an aliquot part of the liquid thus obtained, and in another aliquot part the amount of 'amino'-nitrogen can be determined by treatment with nitrous acid in a special apparatus devised for the purpose by van Slyke. A third aliquot part is treated with strong potassium hydroxide solution, and the amount of ammonia which is evolved is estimated. Of the three bases, only arginine evolves ammonia on this treatment, decomposing according to the equation—

$$C_6H_{14}O_2N_4+2H_2O=C_5H_{12}O_2N_2+2NH_3+CO_2$$

From the amount of ammonia evolved, the amount of arginine can be estimated. If reference be made to the formulæ of the three bases, it will be found that arginine contains three-quarters of its nitrogen in a form which will not react with nitrous acid, whereas histidine contains two-thirds in this form; lysine, on the other hand, contains all its nitrogen in the form of amino-groups. From the reaction with potassium hydroxide, the arginine nitrogen (Arg) can be calculated. If D=non-amino-nitrogen (*i.e.* difference between total N and N present in amino-form, as determined by the amount of nitrogen evolved when a fraction of the liquid is treated with nitrous acid) then histidine N$=\frac{2}{3}$(D$-\frac{3}{4}$Arg) and lysine N=total N$-$(Arg+histidine N). For details of the method reference must be made to special text-books.[1] Amongst the amino-acids not precipitable by phosphotungstic acid, proline and oxyproline contain half their nitrogen in a form not set free by nitrous acid. By determining the difference between amino- and non-amino- nitrogen is the fraction of the hydrolysis products not precipitated by phosphotungstic acid, the amounts of these two amino-acids can be estimated.

Other chemical constants have also been suggested, as, for example, the tyrosine factor, or the amount of tyrosine which a given protein yields on tryptic digestion, and which is estimated by titration with potassium bromate solution, whereby the bromo-tyrosine is formed. Histidine probably also reacts with bromate, and the method has not been found so far to be entirely satisfactory. The acid and basic properties of the proteins also vary considerably. Except, however, in the case of such strongly basic substances as the protamines, and such strongly acid substances as caseinogen, the acid and basic functions can only be determined with difficulty, and for this purpose physical methods must be generally employed.

The capacity of the proteins to combine with acids and bases has been investigated by numerous workers. The most recent investigations of importance are those of J. Loeb, which are published in the form of a monograph, 'Proteins and the Theory of Colloidal Behaviour' (New York, McGraw Hill Co., 1922), which contains references to many of the earlier papers dealing with the subject. The acid and basic functions of the proteins is important, and the subject cannot be dealt with in detail in this place; but a good idea of the scope and the literature of this subject can be gained by reference to the monograph quoted, even if the conclusions arrived at therein may not be considered us final.

C. *Biological reactions.*—If a protein be repeatedly injected into an animal (rabbits are generally employed), the serum of that animal acquires the property of precipitating that protein (antigen). This reaction is known as the 'precipitin' reaction. The precipitin yielding serum will give the reaction only with the protein which produced it, or proteins closely allied. The reaction is characteristic rather of the species of the animal from which the antigen is derived than of its actual chemical characteristics. Thus a precipitin-yielding serum

[1] See *e.g.* Plimmer's monograph on the proteins, Part I. Longmans.

obtained by the injection of human blood into rabbits will give a precipitation with any of the proteins derived from the human body, and if the rabbit had been properly 'immunised' with a sufficient number of injections it will precipitate these proteins in very dilute solutions. Proteins derived from a species zoologically allied to a man, such as anthropoid apes, it will precipitate, but only in more concentrated solutions than are necessary to produce a precipitate in the case of proteins of human origin. This 'precipitin' reaction has been employed practically in meat inspection to determine the origin of the meat in sausages and other meat-containing material, when the origin cannot be ascertained by direct inspection. As to the chemical or physical nature of the precipitin reaction little is known.

V. The Conjugated Proteins.

(*a*) The Nucleoproteins.

This important class of proteins is found in most tissues, the nucleoproteins being generally assumed to be the chief constituent of the cell nucleus. They were first systematically investigated by Miescher, who showed that the spermatozoa of salmon and various other fish were composed chiefly of compounds of the strongly basic protamines, with an amorphous acid called nucleic acid. Nucleic acid is the essential non-protein group in this class of conjugated proteins, and is found in combination with other proteins than the strongly basic protamines. The nucleo-proteins can be extracted from tissues, &c., by dilute salt solutions or very dilute alkali. From the solution thus obtained they can be precipitated by dilute acetic acid. It is sometimes advisable to dry the tissues before extracting by treating with gradually increasing concentrations of alcohol, and finally with absolute alcohol and ether. On digesting nucleoproteins with enzymes, the protein part of the molecule is partially hydrolysed and a residue, soluble in alkalis, but insoluble in dilute acetic acid, is obtained, which is termed a nuclein.

Nucleic acid. It is important in this article to give a short account of this acid, which, although not a protein, is found only in combination with proteins to form substances of great physiological importance. As to the number of nucleic acids and the identity of the nucleic acids from various sources, nothing quite definite can be stated at the present time, although Steudel affirms that the nucleic acid obtained from such different sources as fish-spermatozoa and thymus gland of calf are identical. The researches of Levene indicate, however, that the plant nucleic acids differ from the animal nucleic acid; the former yields on hydrolysis a pentose, whereas the latter yields apparently a hexose, which is broken down during the hydrolytic process into lævulinic acid. The nucleic acid obtained from wheat embryo and yeast appear to be identical.

Nucleic acid was originally obtained by Miescher by treating the nucleoprotein from fish spermatozoa with sodium hydroxide solution and throwing the solution of sodium nucleate thus obtained into an ice-cold solution of hydrochloric acid in alcohol. The operations must be carried out rapidly, as the nucleic acid is readily decomposed by mineral acids. The acid is, however, more stable in the presence of alkalis, and is now generally prepared directly from tissues, &c., without previously isolating the nucleoprotein. Thymus gland gives the largest yield. The gland is boiled with alkali, the hydrolysis mixture, after solution of the proteins, neutralised with acetic acid, and the filtrate from the precipitate thus obtained, thrown into alcohol, whereby sodium nucleate is precipitated; this is purified by solution in water and reprecipitation by alcohol. The free acid can be obtained from the sodium salt by alcoholic hydrochloric acid. Nucleic acid is a strong acid, which gives soluble alkali salts from solutions of which the free acid can be precipitated by mineral acids, but not by acetic acid. A 5 p.c. solution of sodium nucleate forms a gel. On hydrolysis with acids it yields the following groups of substances: (*a*) alloxuric bases, guanine, adenine, xanthine, and hypoxanthine; (*b*) pyrimidine bases, cytosine, uracil, and thymine; (*c*) carbohydrate derivatives, formic and lævulinic acids, decomposition products of hexose; (*d*) phosphoric acid and ammonia. Of these products, xanthine, according to Steudel, is a secondary decomposition product produced by the action of acids on guanine, with scission of ammonia, and hypoxanthine and uracil are in a similar way produced from adenine and cytosine respectively. Steudel represents the hydrolysis of nucleic acid as follows:

$$C_{43}H_{57}N_{15}O_{30}P_4 + 8H_2O + 2O = \underset{\text{(Guanine)}}{C_5H_5N_5O} + \underset{\text{(Adenine)}}{C_5H_5N_5}$$
$$+ \underset{\text{(Thymine)}}{C_5H_6N_2O_2} + \underset{\text{(Cytosine)}}{C_4H_5N_3O} + 4\underset{\text{(Hexose)}}{C_6H_{12}O_6} + 4HPO_3$$

According to this scheme, nucleic acid is a tetra-metaphosphoric acid, containing for each atom of phosphorus a hexose group (compare the glycerophosphates) and one molecule of a base. Recent researches of Levene and his pupils indicate that the ordinary nucleic acid is formed by the coupling up of single groups, termed nucleotides, each of which consists of a phosphoric acid residue combined with a carbohydrate and a base. The nucleic acid of thymus would be formed from four such groups, each containing a different base. The nucleotides themselves can be broken down, according to the method of hydrolysis, into complexes containing phosphoric acid and a carbohydrate, or into complexes containing carbohydrate and base (Ber. 1908, 41, 1905, 2703; 1909, 42, 335, 1198, 2474, 2469, 2703).

Nucleic acids from yeast, wheat embryos, and other sources have also been investigated. Certain other allied substances, such as guanylic acid (from pancreas) and inosinic acid (from meat extract) have been described, which yield on hydrolysis a pentose instead of hexoses. The pentose which has been isolated in this way has been identified by Levene and his co-workers as the hitherto undiscovered sugar *d*-ribose. These are possibly nucleotides (*see* papers of Levene already quoted above).

(*b*) The Glycoproteins.

In this group is included a large number of mucilagenous substances, which are widely

distributed in the animal kingdom. Included amongst them are the mucins of egg-white serum, salivary glands, ascitic fluids, &c. They are, for the most part, precipitated from solutions by very weak alkali. Properly speaking, they should not perhaps be classed as conjugated proteins, as they yield on vigorous hydrolysis the amino-sugar glucosamine—

$$\begin{array}{c} H\ \ H\ \ OH \\ CH_2(OH)C—C—O—CH(NH_2)CHO \\ OH\ OH\ H \end{array}$$

This is a reducing substance, and is probably combined in the molecule in a similar way to that in which the amino acids are combined, and cannot be separated from the conjugated amino acid groups by gentle treatment in the same manner, for example, as globin can be separated from hæmo-globin. It has been already stated that many crude proteins give reactions characteristic of a carbohydrate group (*see Protein reactions*). This is due to the fact that the crude proteins are often contaminated with these mucin-like glycoproteins.

In addition to these, another class of substance is also included amongst the glycoproteins, which are derived chiefly from cartilage and tendons. These contain the group chondroitin sulphuric acid. The constitution of this substance has been investigated by Levene and his co-workers, and forms the subject of several papers in the J. Biol. Chem.

The chemistry of all substances included amongst the glycoproteins may be stated to be still in a very elementary condition.

(*c*) The Hæmoglobins.

These contain the prosthetic group hæmin, which can be separated in the form of the hydrochloride hæmatin from the protein globin by very dilute acid. The hæmins are apparently closely allied to other natural pigments, especially chlorophyll.

VI. The Derived Proteins, and the Hydrolysis of Proteins by Enzymes.

Whilst hydrolysis with strong hot acid solutions leads to the degradation of proteins into simple amino acids, hydrolysis with more dilute acids or alkalis at lower temperatures leads to the formation of products in which two or more amino acids remain conjugated together, forming, according to the degree of complexity, peptides, peptones, proteoses (formerly called albumoses), and proteans (acid and alkali albumens). These products can also be obtained by hydrolysis with proteoclastic enzymes, which are widely distributed both in the animal and vegetable kingdoms. The principal amongst the former are pepsin, from the glands of the stomach, which acts in acid solution; trypsin, from the pancreas, which acts in alkaline solution; and erepsin, from the small intestine, which acts best in nearly neutral solution. The different enzymes produce differing degrees of hydrolysis, each enzyme producing a complex mixture. In a few cases only has a homogeneous product formed from the conjugation of two or more amino acids been isolated from the digestion products. The hydrolytic action of pepsin is the least of the proteoclastic enzymes of the digestive tract; trypsin has a stronger hydrolytic power, whereas erepsin can convert the already relatively simple peptones into simple amino acids. The separation of the enzymatic hydrolysis products into separate fractions is a purely arbitrary one, depending on the precipitation by salts of various concentrations. Thus, for example, Witte's pep tones, a commercial product, obtained by the action of pepsin on fibrin, has been separated into the following fractions by zinc sulphate: from (2 p.c. solution): Fraction I., precipitation commences with 30 p.c. saturation, and is complete at 46 p.c.; Fraction II., precipitated between 58 and 64 p.c. saturation; Fraction III., precipitated between 72 and 82 p.c. saturation; Fraction IV., precipitated between 86 and 100 p.c. saturation. In addition to these, the product also contains fractions which are not precipitated by salts, and simple amino acids. As already stated, separation by salt fractionation is a very incomplete process. Various names have been given to such fractions (primary albumose, secondary albumoses A, B, and C). Similar arbitrary separations by graded strength of alcohol have also been effected. The more complex the hydrolysis products, the more readily are they precipitated by salt solutions; but little progress can be expected in the isolation of the complex intermediary hydrolysis products, which still possess the distinct characteristics of proteins, until new methods for the separation of colloids have been discovered.

Other methods for following the course of protein degradation by enzymes have been employed, amongst which may be mentioned the measurements of changes of viscosity and electrical conductivity of the hydrolysis mixtures, and above all Sörensen's titration method. When an amino acid is treated with formaldehyde, the latter, according to Schiff, acts on the amino group to form a methyleneimino derivative. This is a fairly strong acid, owing to the elimination of the amino group, and can be titrated with alkalis in the presence of phenolphthalein. As hydrolysis of the protein proceeds, scission of amino acids takes place according to the scheme—

$$-CH—NH—CO-+H_2O=-CH\cdot NH_2+COOH-$$

The hydrolysis products increase in acidity after treatment with formaldehyde. In this way the relative number of amino groups set free by hydrolysis can be determined. The increase in the number of free amino groups set free by digestion can also be estimated by treatment with nitrous acid in the apparatus of van Slyke, to which reference has already been made. Also, with increasing hydrolysis, the viscosity and electrical conductivity of the mixture alter.

The enzymes have a special predilection for certain groups; thus, for example, the tryptic enzyme causes a rapid scission of the tryptophan group. This specific action depends, furthermore, not only on the chemical structure of the group, but also on the stereo-chemical configuration of the group and of the whole molecule. The action of various proteoclastic enzymes on the synthetic polypeptides has formed the subject of exhaustive study by Abderhalden and his

pupils, which are described in numerous papers (Zeitsch. physiol. Chem.).

Other derivatives of proteins have been described which are obtained by the action of chemical reagents. Thus the halogens, especially chlorine and bromine, readily react with the proteins. Nitrous acid also reacts. It is difficult to say, however, whether the various substances thus obtained are chemical entities.

Although general protein chemistry may be still considered in its infancy, the literature of the subject is already extensive. Various aspects have, however, been summarised in a large number of recent monographs, to which the reader is referred for more detailed information.

Bibliography.—Abderhalden: Biochemische Arbeitsmethoden, Berlin, 1910. Numerous articles on the methods of preparation and general chemistry of simple and conjugated proteins.

Oppenheimer: Handbuch der Biochemie, Jena, 1908. Also contains articles by various authors.

Aders Plimmer and Hopkins (edited by), Monographs on Biochemistry, 1908, R. H. Aders Plimmer, Chemical Constitution of the Proteins (two parts); Osborne, The Vegetable Proteins; Schryver, The General Characters of the Proteins.

Emil Fischer's collected papers (Untersuchungen über Aminosäuren, &c., Berlin, 1910) deal chiefly with the isolation and synthesis of amino acids and the synthesis of the peptides.

S. B. S.

PROTOCATECHUIC ACID. Six dihydroxybenzoic acids are possible theoretically, and all are known. Of these protocatechuic acid is the most important.

Protocatechuic acid, 3 : 4-*Dihydroxybenzoic acid.* This acid is of interest from the number of vegetable principles from which it may be obtained and which may therefore be regarded as containing the same grouping of the substituted radicles in the benzene nucleus. It is formed by fusing with potash oil of cloves, vanillin, piperic, caffeic, ferulic, hemipinic, and other acids, apiin (a substance present in parsley), quercetrin, kalotannin, Quebracho Colorado gum, and a large number of natural resins (Barth, Annalen, 154, 364; 159, 232; Hlasiwetz and Barth, *ibid.* 130, 346; 134, 277; 139, 78; Hlasiwetz and Grabowski, *ibid.* 139, 96; Hlasiwetz and Pfandler, *ibid.* 127, 357; Hesse, *ibid.* 112, 52; 122, 221; Fittig and Macalpine, *ibid.* 168, 111; Fittig and Remsen, *ibid.* 159, 129; Strecker, *ibid.* 118, 311; Offermann, *ibid.* 280, 24; Beckett and Wright, J., 1876, 808; Kraut and Dellder, Annalen, 128, 285; Malein, *ibid.* 134, 118; Perkin, Chem. Soc. Trans. 1897, 811; 1900, 424; Knox and Prescott, J. Amer. Chem. Soc. 1898, 20, 34; Arata, Chem. Soc. Abstr. 1878, 986). It is also formed by treating quinic acid with the mould *Micrococcus chinicus* (Löw, Ber. 1881, 453; Emmerling and Abderhalden, Centr. Bakt. Par. 1903, 10, 337). Protocatechuic acid may be prepared by gradually adding East Indian kino as a fine powder to 3 parts of fused potash. When the mass becomes light orange in colour, it is poured on to a cold plate to cool, then broken up and dissolved in hot water containing a little dilute sulphuric acid. After standing for 24 hours, sodium sulphate crystallises out. The liquid is filtered off and extracted with ether. The ether is evaporated off and the crude acid recrystallised from hot water (Stenhouse, Chem. Soc. Trans. 1875, 8). According to Hlasiwetz and Barth (Annalen, 130, 340), the acid is best purified by precipitating the lead salt with lead tartrate and subsequently decomposing the salt with hydrogen sulphide. It may also be prepared by heating 1 part of catechol, 4 parts of ammonium carbonate, and 5 parts of water in sealed tubes at 130°–140° (Miller, Chem. Soc. Trans. 1882, 399); by the action of potassium persulphate on *p*-hydroxybenzoic acid in alkaline solution (Chem. Farb. Schering. D. R. P. 81298; Frdl. iv. 121); by condensing chloracetic acid with eugenol and heating the product with caustic alkali at 230°–250° (Lederer, D. R. P. 80747; Frdl. iv. 151); by fusing *p*-chlor- or *p*-brom-*m*-hydroxybenzoic acid with caustic alkali at 180°–200° (Merck. D. R. PP. 71260, 74493; Frdl. iii. 849; Ber. Ref. 1894, 531); by treating piperonaldehyde with chlorine (3 mols.) in carbon tetrachloride, evaporating the solvent when the colour has disappeared, decomposing the residue with water when, after boiling, the pure acid separates, on cooling, in quantitative yield:—

$CH_2O_2 : C_6H_2 \cdot CHO + 3Cl_2 \rightarrow CCl_2O_2 : C_6H_2 \cdot COCl$;

this $+3H_2O \rightarrow C_6H_3(OH)_2.CO_2H$ (Schmidt, D. R. P. 278778). Protocatechuic acid crystallises in colourless prismatic needles, m.p. 199°. Readily soluble in boiling, less soluble in cold water; very soluble in alcohol, less soluble in ether. Crystallises from hot water with 1 molecule of water of crystallisation, which it loses on heating to 105°. Heat of solution of anhydrous acid, −5·82 cal. (Massol, Bull. Soc. chim. 1900, [iii.] 23, 231; Imbert, *ibid.* 832; Berthelot, Compt. rend. 101, 541). Decomposes on distillation or on heating with potash into carbon dioxide and pyrocatechol. Bromine in the cold reacts to yield bromoprotocatechuic acid (Barth, Annalen, 142, 246), but excess of bromine at 100° yields hydrogen bromide, carbon dioxide, and tetrabromopyrocatechol $C_6H_2Br_4O_2$ (Stenhouse, Chem. News, 29, 95; Chem. Soc. Trans. 1875, 7). Nitrous acid converts protocatechuic acid into oxalic and carboxytartronic acids ($C_4H_6O_8$), small quantities of picric acid, 2 : 4-dinitrophenol, 3 nitro-*p*-hydroxybenzoic acid, and dinitrohydroxyquinone (Grube, Ber. 12, 514). By electrolytic oxidation in dilute sulphuric acid solution catellagic acid is formed (A. G. and F. M. Perkin, Chem. Soc. Trans. 1908, 1196). By heating protocatechuic acid with 2 parts of benzoic acid and 50 of sulphuric acid (66°B.) at 140°, a deep brown substance is obtained, producing with mordants almost the same shades as with alizarin; it is probably rufiopine

$$C_6H_2(OH)_2 \begin{matrix} CO \\ CO \end{matrix} > C_6H_2(OH)_2$$

(Noelting and Bourchart, Bull. Soc. chim. [ii.] 37, 394). By heating it with pyrocatechol or resorcinol and zinc chloride at 150°, isomeric tetrahydroxydiphenylketones are obtained, which can be used to dye and print chrome mordanted cotton (Farb. Meister, Lucius, and Brüning, Eng. Pat. 19847; J. Soc. Chem. Ind. 1892, 902).

Protocatechuic acid gives with ferric chloride an intense bluish-green coloration, which on addition of sodium carbonate changes to deep

red (*v.* also PYROCATECHOL) (Lutz, Chem. Zeit. 31, 570).

α-Resorcylic acid, 3 : 5-*Dihydroxybenzoic acid.* Prepared by fusing 1 : 3 : 5-disulphobenzoic acid with potash (Barth and Senhofer, Annalen, 159, 222; Hopfgartner, Monatsh. 14, 685); m.p. 232°–233° (B. and S.), 225°–227° (H.); sparingly soluble in cold water, very soluble in hot water, alcohol, or ether; gives no coloration with ferric chloride. On warming α-resorcylic acid with 4 parts of sulphuric acid at 140°, it dissolves with a deep red colour, addition of water changes the colour to green, flocks of anthrachrysone $C_{14}H_8O_6$ being formed, and if it is heated with benzoic acid in addition to sulphuric acid, xanthopurpurin $C_{14}H_8O$ is also formed. Oxidation with persulphate in concentrated sulphuric acid gives a yellow dyestuff (Bad. Anil. und Soda Fab. D. R. P. 85390; Frdl. iv. 360). Azo dyestuffs with amino-carboxylic acids *v.* Bayer and Co. D. R. P. 60500; Frdl. iii. 620; blue oxazine dyestuffs with nitrosodialkylanilines *v.* Bad. Anil. und Soda Fab. D. R. P. 57938; Frdl. iii. 370.

Pyrocatechol-*o*-carboxylic acid 2 : 3-*Dihydroxybenzoic acid.* Prepared by fusing 3-iodosalicylic acid with potash (Miller, Annalen, 220, 126) or in small quantities, together with protocatechuic acid, by heating catechol, ammonium carbonate and water at 140° (Miller, *ibid.* 116), m.p. 204°.

3-*methyl ether* (*guaiacolcarboxylic acid*). Prepared by the action of carbon dioxide on the hot alkali salts of guaiacol (Heyden. Nachf. D. R. P. 51381; Frdl. ii. 132); m.p. 152° (Fritsch, Annalen, 301, 354).

β-Resorcylic acid, 2 : 4-*Dihydroxybenzoic acid.* Prepared by fusing *p*-cresolsulphonic acid with potash (Ascher, Annalen, 161, 11); by heating resorcinol with ammonium carbonate and water at 120°–130° (Brunner and Senhofer, Ber. 1880, 2356); by fusing β-resorcylaldehyde or umbelliferone with potash (Tiemann and Reimer, Ber. 1879, 997; Tiemann and Parrisius, *ibid.* 1880, 2358); by heating 20 grms. resorcinol with 100 grms. potassium bicarbonate and 200 grms. water for 1½ hours on the water-bath, saturating with hydrogen chloride and extracting with ether. The ethereal solution is shaken with sodium hydroxide, the aqueous layer drawn off, acidified, and re-extracted with ether (Bistrzycki and Kostanecki, Ber. 1885, 1985). M.p. (anhydrous) 213°; readily soluble in warm water, alcohol, or ether; aqueous solution is coloured violet on addition of a little calcium chloride solution, the colour changing to yellow-brown on addition of more calcium chloride. For methylation *v.* Gregor, Monatsh. 16, 882. For 3-bromo-β-resorcylic acid and 3-bromo-5-amino-*B*-resorcylic acid and their salts, *v.* Hemmelmayr, Monatsh. 1914, 35, 1. For *o*-Benzoyl derivatives, *v.* Bergmann and Dangschat, Ber. 1919, 52, [B] 371.

Gentisic acid, *Hydroquinonecarboxylic acid, Quinolcarboxylic acid,* 2 : 5-*Dihydroxybenzoic acid.* Prepared by fusing 5-iodosalicylic acid with potash (Lautemann, Annalen, 12, 311; Liechti, *ibid.* Suppl. 7, 144; Demoli, Ber. 1874, 1438; Goldberg, J. pr. Chem. [ii.] 19, 371; Miller, Annalen, 220, 124), and similarly from the bromo compound (Rakowski and Leppert, Ber. 1875, 789); by the action of nitrous acid on 5-aminosalicylic acid (Goldberg, *l.c.*); by fusing gentisin with potash (Hlasiwetz and Habermann, Annalen, 175, 66); by heating hydroquinone, potassium bicarbonate and 4 parts of water to 130° and subsequently treating it with potassium sulphite (Senhofer and Sarlay, Monatsh. 2, 448); by treating *p*-dihydroxyphthalimide with strong hydrochloric acid (Thieler and Meisenheimer, Ber. 1900, 676); and by oxidising salicylic acid with potassium persulphate in alkaline solution (Chem. Fabr. Schering. D. R. P. 81297; Frdl. iv. 127), m.p. 200°; readily soluble in water, alcohol, or ether; insoluble in chloroform and benzene (Tiemann and Müller, Ber. 1881, 1988). Dry distillation yields carbon dioxide and hydroquinone. Ferric chloride gives a deep blue colour; when heated, gentisic acid reduces Barreswil's (Fehling's) solution. Oxidation with manganese dioxide and sulphuric acid, *v.* Juch, Monatsh. 1905, 26, 839. Bromo derivatives, *v.* Hemmelmayr, Monatsh. 1909, 30, 255.

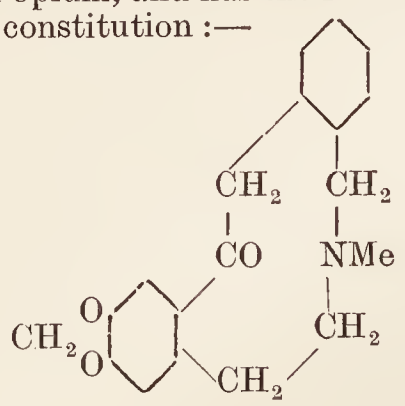
5-*methylether* is prepared by treating the acid with 2 mols. of potassium hydroxide and 2 mols. of methyl iodide (Kostanecki and Tambor, *ibid.* 16, 920); m.p. 141°–142°.

2 : 6-Dihydroxybenzoic acid. Formed together with 2 : 4-dihydroxybenzoic acid by heating resorcinol with 4 parts ammonium carbonate and 5 parts water at 120°–130° (Senhofer and Brunner, Ber. 1880, 2356); decomposes without melting at 148°–167° into carbon dioxide and resorcinol. On adding a small quantity of ferric chloride a violet colour is produced, changing to blue with a further quantity of the reagent.

PROTON. The term applied to the positively charged particles contained in the atoms.

PROTOPINE *v.* OPIUM.

PROTOPINE $C_{20}H_{19}O_5N$ (*Fumarine, Macleyine*) is widely distributed in plants of the N. O. *Papaveraceæ* and *Fumariaceæ, e.g.* in *Chelidonium majus* (Linn.) (Schmidt and Selle, Arch. Pharm. 1890, 228, 441), *Sanguinaria canadensis* (Linn.) (König and Tietz, *ibid.* 1893, 231, 145, 161), *Bocconia cordata* (Willd.) (Eykman, Rec. trav. chim. 1884, 3, 182), opium (Hesse, Annalen, 1872, S. 8, 318), *Adlumia cirrhosa* (Rafin.), *Glaucium flavum* (Crantz.), *Corydalis* spp., *Dicentra* spp., &c. (*cf.* Schmidt, Arch. Pharm. 1901, 239, 395; 1911, 249, 224; Fischer and Soell. Ph. Ar. 1902, 5, 121; Heyl, Arch. Pharm. 1903, 241, 313; Asahina, *ibid.* 1909, 247, 201; Danckwortt, *ibid.* 1912, 250, 590). Monoclinic crystals, m.p. 207°. Tertiary base. The salts are crystalline; the aurichloride $B{\cdot}HAuCl_4$, amorphous, melts at 182°. Protopine gives with sulphuric acid a blue-violet coloration, changing to green. According to W. H. Perkin (Chem. Soc. Trans. 1916, 109, 819) protopine is closely related to cryptopine, which it accompanies in opium, and has the following somewhat unusual constitution :—



G. B.

PROTOSAL *v.* SYNTHETIC DRUGS.

PROTOSIL. A silver protein compound, used as an antiseptic.

PROTOVERATRIDINE, PROTOVERATRINE *v.* CEVADINE.

PROUSTITE, or light-red silver-ore (Ger. *Lichtes Rothgiltigerz*; Span. *Rosicler claro*). Silver sulpharsenite Ag_3AsS_3 crystallised in the rhombohedral system. It forms transparent scarlet crystals with a brilliant adamantine lustre, which soon blacken on exposure to sunlight. The scarlet steak serves to distinguish proustite from the closely allied mineral pyrargyrite (*q.v.*). Hardness $2\frac{1}{2}$; sp.gr. 5·57. It occurs sparingly in metalliferous veins, but at Chañarcillo in Chile is of importance as an ore of silver (Ag 65·4 p.c.). Named after the French chemist J. L. Proust (1754–1826), who distinguished it from pyrargyrite. L. J. S.

PRULAURASIN *v.* GLUCOSIDES.

PRUNETIN. The bark of the *Prunus serotina* (Ehrh.) contains a glucoside *prunitrin* $C_{22}H_{24}O_{11},4H_2O$, fine needles, which when hydrolysed with boiling dilute hydrochloric acid yields prunetin and glucose.

The bark of a spurious substitute for that of the *Prunus serotina*, probably *P. emarginata*, has been shown by Finnemore (Pharm. Jour. 1910, [iv.] 31, 604) to contain prunitrin in addition to guercimeritrin (Parkin, Chem. Soc. Trans. 1909, 95, 243).

Prunetin $C_{15}H_9O_4{\cdot}OCH_3$, colourless needles, m.p. 242, dissolves in alkalis with a slight yellow colour, and is sparingly soluble in all the usual solvents. *Monacetylprunetin* $C_{16}H_{11}O_5(C_2H_3O)$, pale yellow needles, m.p. 190°; *diacetylprunetin* $C_{16}H_{10}O_5(C_2H_3O)_2$, m.p. 224°–226°; *benzoylprunetin* $C_{16}H_{10}O_5(C_7H_5O)_2$, needles, m.p. 215°; *methylprunetin* $C_{15}H_8O_3(OCH_3)_2$, needles, m.p. 145°; and *acetylmethyl prunetin*

$$C_{15}H_7O_3(OCH_3)_2C_2H_3O$$

have been prepared.

Fused with caustic potash at 250°, prunetin gives *phloroglucinol* and p-*hydroxyphenylacetic acid.*

Prunetol $C_{15}H_{10}O_5$, colourless needles, m.p. 290°, is formed by the demethylation of prunetin with hydriodic acid, and yields *acetylprunetol* $C_{15}H_7O_5(C_2H_3O)_3$, and *prunetol sulphate*

$$C_{15}H_{10}O_5{\cdot}H_2SO_4$$

yellow needles. On methylation with methyl iodide *prunetol dimethyl ether* identical with prunetin monomethyl ether, and a sparingly soluble methyl ether, the acetyl derivative of which melts at about 186°, are produced (Finnemore, Chem. Soc. Trans. 1910, 98, 1102).

A. G. P.

PRUNICYANIN *v.* ANTHOCYANINS.

PRUNISIN *v.* GLUCOSIDES.

PRUSSIAN BLUE *v.* CYANIDES.

PRUSSIAN BROWN *v.* PIGMENTS.

PRUSSIAN RED or **VENETIAN RED** *v.* PIGMENTS.

PRUSSIATE OF POTASH *v.* CYANIDES.

PRUSSIC ACID *v.* CYANIDES.

PSEUDACONITINE *v.* ACONITINE.

PSEUDOCAPROIC ACID *v.* CAPROIC ACIDS.

PSEUDOCUMENE *v.* CUMENES.

PSEUDOCUMENOL *v.* PHENOL AND ITS HOMOLOGUES.

PSEUDOJERVINE *v.* CEVADINE.

PSEUDOMORPHINE, PSEUDOPAPAVERINE *v.* OPIUM.

PSEUDO-WOLLASTONITE *v.* WOLLASTONITE.

PSILOMELANE. An abundant ore of manganese, readily distinguished from the other black oxides of manganese (pyrolusite, manganite, and wad) by its greater hardness (H. = $5\frac{1}{2}$) and its characteristic mamillated, botryoidal, and stalactitic forms. It is variable and complex in composition, containing MnO_2 70–83, MnO 3–8, H_2O 3–6 p.c., together with smaller but widely varying amounts of barium (BaO up to 16 p.c.), potassium (K_2O to 6 p.c.), &c. Sp.gr. 3·7–4·7. Adopting the suggestion of Laspeyres (1876) of the hypothetical acid H_4MnO_5, L. L. Fermor (Mem. Geol. Survey, India, 1909, xxxvii.) regards the mineral as a manganate with the general formula—

$$mR_2'MnO_5+nR_4'''(MnO_5)_3$$

where R″ = Mn, Ba, K_2, H_2, (Fe, Ca, Mg, Na_2, Co, Ni, Cu, Zn), and R‴ = Mn, Fe, (Al). Lacroix, on the other hand, places the mineral in his group of manganites and separates romanechite (from Romanèche, France) as a distinct species with the formula $H_2(Mn,Ba)Mn_3O_8$, that of ordinary psilomelane being given as

$$xRO{\cdot}yMnO_2{\cdot}zH_2O$$

The name psilomelane (from ψιλός, naked, and μέλας, black) is descriptive of the smooth, black, and shining surfaces of the mineral, and the German name *Schwarzer Glaskopf* also refers to this characteristic appearance. The mineral has a brownish-black streak, and breaks with a smooth fracture, with sometimes indications of a fibrous crystalline structure. Fermor has separated distinctly crystallised varieties of the Indian mineral under the name hollandite (*q.v.*). Psilomelane has the same mode of occurrence as pyrolusite (*q.v.*), and the two minerals are mined together in large quantities. In India it is the most abundant of the manganese ores. L. J. S.

PSITTACINITE. Basic vanadate of lead and copper, perhaps $(Pb,Cu)_3V_2O_8{\cdot}(Pb,Cu)(OH)_2$, containing 17–22 p.c. V_2O_5, and with lead and copper in approximately the ratio 1 : 1. A small amount of zinc replaces copper. The composition is thus analogous to that of descloizite (*q.v.*), but with copper in place of zinc; an intermediate member is represented by the variety cuprodescloizite. *Mottramite* (with 17·14 p.c. V_2O_5), for which Roscoe gave the formula $(Pb,Cu)_3V_2O_8{\cdot}2(Pb,Cu)(OH)_2$ is probably identical with psittacinite. The compact earthy mineral is siskin- to olive-green in colour, hence the name, from psittacinus, parrot-green; but the crusts of minute crystals are dark greenish-black with a velvety appearance. Sp.gr. 5·89 (for mottramite). The original material was found with lead and copper ores and gold in the Silver Star district in Montana. It is also found near Las Cortaderas in Argentina, Bisbee in Arizona, and with copper and lead ores at Tsumeb near Otavi in South-West Africa. Mottramite occurs as a crust of minute crystals on the cupriferous Keuper sandstone at Alderley and Mottram St. Andrew in Cheshire. The vanadium and copper present in sedimentary rocks (compare

also the occurrence of hydrated copper vanadate, volborthite, in the Permian formation of Russia) is probably of organic origin, since these elements have been detected in the blood of certain organisms where they function as iron.

L. J. S.

PSYCHOTRINE *v.* IPECACUANHA.

PTERITANNIC ACID *v.* FILIX MAS.

PTOMAINES, *v.* PUTREFACTION BASES.

PTYALIN *v.* DIASTASE.

PUCHERITE. Bismuth vanadate, $BiVO_4$, crystallised in the orthorhombic system. It forms crusts of small, reddish-brown, brilliant crystals on ores of bismuth. Sp.gr. 6·25. It is found in the Pucher mine at Schneeberg and at other places in Saxony; and has also been recorded from Western Australia and Madagascar. A yellow pulverulent 'bismuth-ochre' occurring with native bismuth in the gem (tourmaline) and lithia mines at Pala in San Diego Co., California, has been found to have the same composition. L. J. S.

PULEGENONE, PULEGONE *v.* KETONES.

PULMOFORM *v.* SYNTHETIC DRUGS.

PUMICE, or **Pumice-stone.** A frothy form of volcanic glass, formed by the expansion of occluded water-vapour when the molten lava flowed out at the earth's surface. The glassy obsidian (*q.v.*), invariably associated with pumice, represents the same magma which had consolidated under a somewhat greater pressure. This is proved by the fact that fragments of obsidian when heated in a crucible to the point of fusion suddenly swell up, and are converted into pumice. An artificial pumice may be made by blowing steam or air through molten slag or glass. Volcanic lavas of various kinds may assume the pumiceous form, but it is only those richer in silica (corresponding with rhyolite and obsidian, *v.* LAVA) that yield a pumice of economic value. The following analyses are given by G. P. Merrill (The Non-Metallic Minerals, 2nd edit., 1910): I of pumice from Capo di Costagna, Lipari Islands; II of pumice-dust from Orleans, Harlan Co., Nebraska:—

	SiO_2	Al_2O_3	Fe_2O_3 / FeO	CaO	MgO	K_2O	Na_2O	Loss on ignition	Total
I.	73·70	12·27	2·31	0·65	0·29	0·73	4·25	1·22	99·42
II.	69·12	17·64		0·86	0·24	6·64	1·69	4·05	100·24

Owing to its cellular structure, pumice floats on water, but the sp.gr. of the powdered material is 2·3 to 2·4 The vesicules are either round or elongated (due to the flowing of the lava), and the glass has the form of thin partitions or threads. It is on this peculiarity of structure that the abrasive qualities of the material depend. The presence of minute crystals of felspar, &c., is detrimental, since, being harder, these produce scratches on the work. Blocks of pumice are used for cleaning and smoothing; but with coach-builders, &c., it is now, to a certain extent, replaced by an artificially prepared stone. Powdered pumice or pumice-dust is used in the manufacture of metal polishes and scouring soaps. This is often mistaken for diatomaceous earth or diatomite (*q.v.*), from which it may readily be distinguished under the microscope (pumice powder consisting of irregular, glassy fragments) and by chemical tests (diatomite being a hydrated silica soluble in caustic soda solution).

Pumice is found in several volcanic districts, but the chief commercial source for the better qualities of material is in the Lipari Islands north of Sicily. The best material is from Campo Bianco, Monte Pelato, and Monte Chirica on Lipari. On this island there are some 170 quarries and mines producing about 6000 tons of pumice per annum. The price varies from 30 to 3000 lire per ton, being usually 350 to 500 lire for assorted material. An inferior grade, called 'alessandrina,' is used in brick-shaped pieces for smoothing oilcloth. Small quantities of pumice are also exported from Teneriffe. In the United States enormous beds of pure white pumice-dust are found over wide areas in Nebraska, Kansas, California, Idaho, Utah, South Dakota, Wyoming, Oregon, Colorado, Oklahoma, and Iowa. The annual production amounts to about 10,000 tons, and comes chiefly from Harlan and Lincoln counties, Nebraska. This material is of the nature of a volcanic ash or dust, the lava having been blown into fine fragments by the expanding water-vapour and scattered by the winds. It is largely used for polishing powders and soaps; other suggested applications are for non-conducting packings, fireproof material, cements, and cheaper glassware. L. J. S.

PUMPKIN, *Cucurbita Pepo* (Linn.). A plant growing in warm climates, yielding large fruits which are used as a vegetable and for stock feeding. Many varieties are known. Of the whole fruit, from 50 to 70 p.c. consists of rind and seeds, which are not edible. König gives as the average composition of the flesh—

Water	Protein	Fat	Sugar	Other N-free extract	Crude fibre	Ash
90·3	1·1	0·1	1·3	5·2	1·2	0·7

American analyses show a higher water content, 93 or 94 p.c.

Pumpkin seeds contain from 25 to 35 p.c. of oil. Power and Salway (J. Amer. Chem. Soc. 1910, 32, 346) have examined the seeds with a view of discovering the constituent to which the action as a vermifuge, which the seeds possess, is due. They showed that no constituent of the seeds possessed any marked physiological activity and conclude that any medicinal value which they may have must be attributed to a mechanical effect. They found the seeds to consist of 20·8 p.c. of husks and 79·2 p.c. of kernels.

The entire seed yielded to light petroleum 34·3 p.c. of oil, which was optically inactive, had a sp.gr. of 0·9220 at 20°/20°, acid value 3·4, saponification value 189·4, iodine value 119·7. It consisted of the glycerides of linolic acid (45 p.c.), olcic acid (25 p.c.), and palmitic and stearic acids (30 p.c.), together with small quantities of a phytosterol $C_{27}H_{46}O$, m.p. 162°–163°, and a similar substance, m.p. 140°.

From the press cake, after removal of the oil, they obtained some soluble proteid material, sugar, traces of salicylic acid and of copper and about 0·06 p.c. of a resin, in which they found an acid, $C_{25}H_{51}O{\cdot}COOH$, m.p. 99°, soluble in hot alcohol and in ethyl acetate. It yielded an ethyl ester melting at 61°. Physiological tests with

both the fatty oil and the resin, showed that neither possessed any value as a tænifuge.

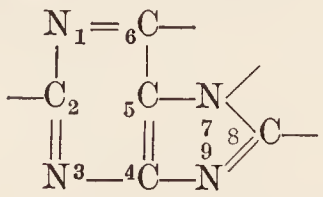
H. I.

PURGATIN (purgatol) *v.* SYNTHETIC DRUGS.

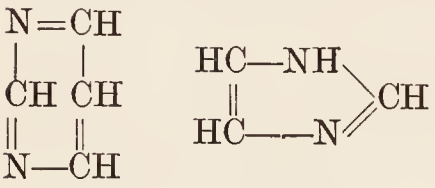
PURGEN. Trade name for phenolphthalein used as a laxative.

PURGING NUT TREE OIL. The tree, *Jatropha Curcas* (Linn.), is related to the castor and croton oil plants. The dry seeds contain from 34 to 37 p.c. of oil. The constants of three samples of oil from different localities varied as follows: d^{15} 0·9183 to 0·9207; sapon. number 191 to 193; iodine number 95·6 to 104·3; acetyl number 18·7 to 25·4; Reichert-Meissl number 0·37 to 0·60; Polenske number 0·22 to 0·24. Heating at 100° for 22 hours discolours the oil, and exposure to light and air for 7 hours introduces a slight drying (Chem. Soc. Abstr. 1922, 122, i. 908).

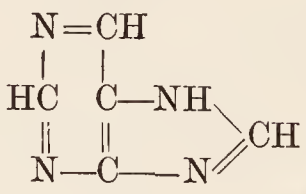
PURINES. The purines form a group of compounds, chiefly of animal or vegetable origin, containing the complex



which may be regarded as a combination of the two simpler ring compounds, the *pyrimidine* or *metadiazine* and the *iminazole* or *glyoxaline*



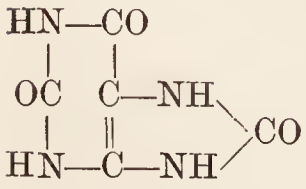
Pyrimidine. Iminazole.



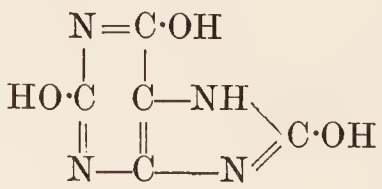
Purine.

The name *purine* (from *purum* and *uricum*) was given by Fischer (Ber. 1898, 31, 2550) to the simplest member of the series, obtained from uric acid by a process of reduction. The naturally occurring purines contain hydroxyl or amino or methyl groups in place of the hydrogen atoms of the purine. For the hydroxyl substituted derivatives, the keto formula I. is more suitable than the tautomeric enolic formula II.

URIC ACID.



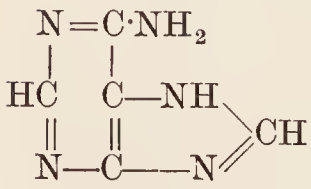
I.



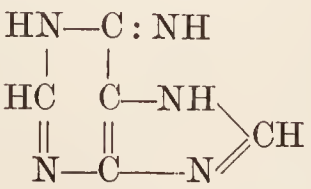
II.

whilst the amino formula III. is adopted for the amino substituted derivatives in preference to the imino formula IV.

ADENINE.

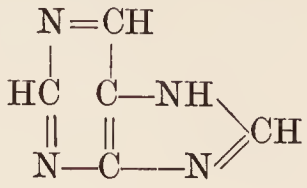


III.

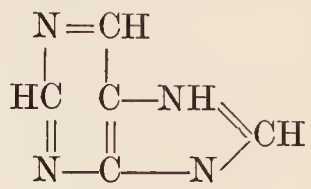


IV.

Purine itself is represented by the formula V. in preference to formula VI., and a similar convention is adopted in respect of its derivatives substituted in positions other than 7, 8, or 9.



V.

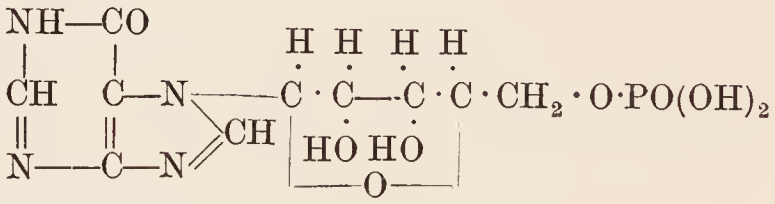


VI.

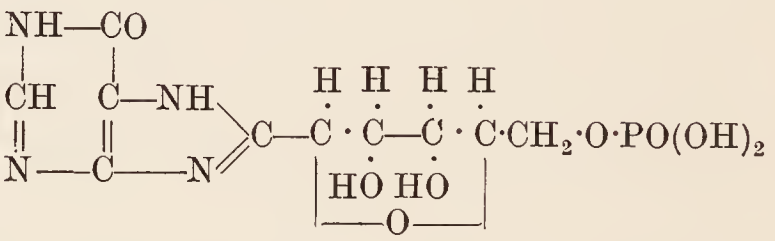
The source of the naturally occurring purines is the nucleoproteins of the cell nucleus. These are compounds of nucleic acids with different proteins, yielding, on partial hydrolysis, the protein and the nucleic acid. The nucleic acids are regarded as mono- or poly-nucleotides, *i.e.* compounds of phosphoric acid conjugated with a complex compound of a carbohydrate (hexose or pentose) and a base (purine or pyrimidine). The molecule of yeast nucleic acid

$$C_{38}H_{49}N_{15}P_4O_{29}$$

is composed of four such nucleotides (Levene and Jacobs, Ber. 1911, 44, 1027). The mono-nucleotide *inosic acid* $C_{10}H_{13}N_4PO_8$, is a compound of phosphoric acid, *d*-ribose and hypoxanthine, and can be represented by the formula



or



(Levene and Jacobs, *ibid.* 746; *cf.* Fischer and Helferich, Ber. 1914, 47, 210; Jones and Read, J. Biol. Chem. 1917, 31, 337).

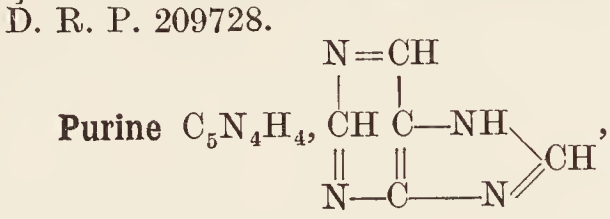
During metabolism the nucleoproteids undergo complete disruption, yielding the purine bases, guanine, adenine, xanthine, and hypoxanthine; and the pyrimidine bases, thymine, cytosine, and uracil. As a result of tissue metabolism, every normal adult excretes a certain characteristic amount (0·1 to 0·2 grm. daily) of purine substances which is independent of the diet, and this may be termed 'endogenous urinary purine,' (*v.* Lambling and Dubois, Compt. rend. soc. biol. 1914, 76, 614). On ordinary diet the amount is increased by a part of the 'nutrition purine' and this may be termed 'exogenous urinary purine.' The nutrition purine does not pass wholly into the urine, a certain fraction remains in the organism, the purine double ring being broken down; thus on a diet of calf's thymus that contains 0·4 p.c. of purine substances, the percentage of 'exogenous urinary purine' is 0·1 p.c. (Burian and Shur, Pflüger's Archiv. 1900, 80, 241). The purine bases are not precipitated from very dilute solutions by phosphotungstic acid, Bass and Wiechowski (Chem. Zentr. 1913, 1, 331; from Wien. klin. Woch. 1912, 25, 1863).

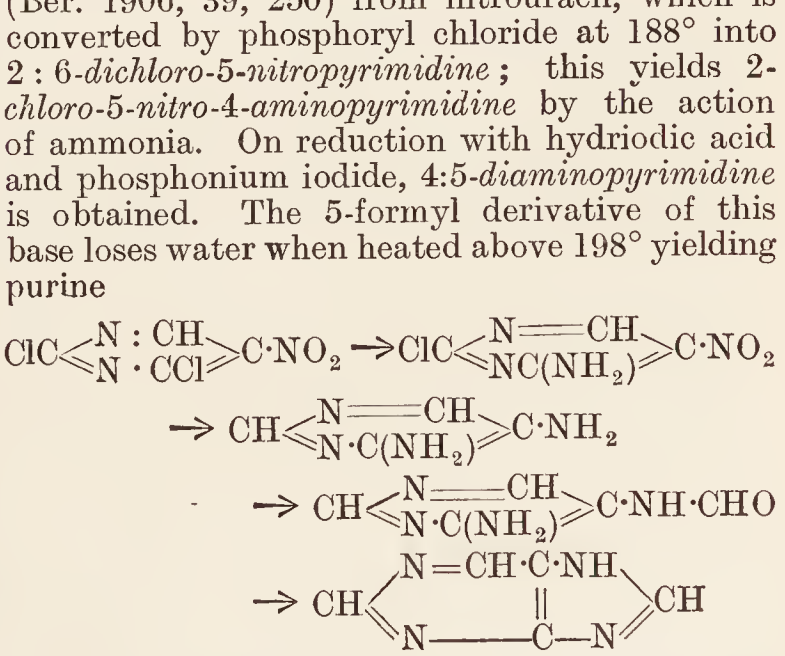
The amino- and oxy- purines occur in both

the animal and vegetable economy, but in plant tissues there are found also methyloxypurines (caffeine, theobromine, etc.); *v.* Johnson (J. Amer. Chem. Soc. 1914, 36, 337) for the suggestion that pyrimidines of the barbituric acid series may be the precursors of purines in plant growth. The methyloxypurines (heteroxanthine, paraxanthine) present in urine form part of the 'exogenous urinary purine' derived from a vegetable diet. Only a small proportion of the methyl purine present in the food is excreted unchanged, most of it undergoes demethylation by a process of oxidation and appears in the urine as a lower methylpurine.

Relation between the structure and the physical properties of the purines. The substitution of hydroxyl or the amino group for the hydrogen atoms of purine causes an increase in the melting-point and a diminution in the solubility of the compound: thus purine melts at 216°, 8-oxypurine at 317°, 6-aminopurine (adenine) at 360°. Purine is readily soluble, 6-oxypurine (hypoxanthine) dissolves in 69·5, 2 : 6-dioxypurine (xanthine) in 1400, 6 : 8-dioxypurine in 270, and trioxypurine (uric acid) in 1850 parts of boiling water; whilst 6-aminopurine (adenine) is very readily soluble in boiling water, 6-amino-2-oxypurine, 2-amino-6-oxypurine (guanine) and 2-amino-6 : 8-dioxypurine are very sparingly soluble, and 2 : 6-diamino-8-oxypurine is soluble in 350 parts of boiling water. The introduction of methyl groups causes a marked increase in the solubility and a lowering of the melting-point, thus whilst xanthine is soluble in 1400 parts of boiling water, and decomposes without melting, caffeine (1 : 3 : 7-trimethylxanthine) dissolves in 2 parts of boiling water, melts at 234°–235°, and sublimes with slight decomposition at 384°. The methyl substituted purines are also much more readily hydrolysed than those that are not so substituted, thus uric acid can be boiled with excess of normal alkali for a long time without undergoing much decomposition, but tetramethyl-uric acid is rapidly decomposed even in the cold, the mono-, di-, and tri-methyl-uric acids standing in intermediate positions between the extremes. The position of the methyl groups in the compound also appears to affect the ease with which the decomposition occurs, the 1 : 3 : 9-trimethyl-uric acid, for example, is much more readily decomposed than the 1 : 7 : 9-derivative (Fischer, Ber. 1898, 31, 3266).

Physiological action of the purines. The action of caffeine and theobromine is twofold, in the first place they act on the central nervous system producing an increased sensibility to external stimulus, developing into tetanus as the dose is increased and culminating in paralysis when the dose is large. Secondly, they act on the muscles, facilitating the contraction of these at first, but producing muscular rigor when the dose is larger. Parallel with the action on the muscles is a diuretic action, the two increasing together. The nervous action depends on the presence of nitrogen in the molecule, for it is exhibited also by ammonia and its salts; the muscular action is characteristic of the purine ring. Purine itself exhibits both actions. Introduction of oxygen or alkyl groups affects the degree of the two actions both absolutely and relatively; no regularities could be observed in this respect, probably owing to the difference in solubility of the drugs. The introduction of alkyloxy groups produces a hypnotic or narcotic action which may almost mask the tetanus (Schmiedeberg, Ber. 1901, 34, 2550). Injected intravenously they diminish or increase the blood-pressure (Degrez and Dorléans, Compt. rend. 1913, 156, 93; *v.* also Golowinski, Arch. ges. Physiol. 1915, 160, 205, for their influence on the circulatory system and on muscular tissue). Nontoxic nucleins are made toxic by purines according to Waele (Zeitsch. Immun. expt. Tharapie, 18, 410, from Amer. Chem. Abs. 1913, 2967), and plant growth and cell division inhibited by strong solutions of purines (Coppin, Bio-Chem. J. 1912, 6, 416). According to Heller (Zietsch. phys. Chem. Biol. 1917, 3, 106) the phenomenon of bioluminescence is associated with the last phases of catabolism of those nitrogenous substances which are eliminated as purines from the animal organism. For preparation of purine derivatives of therapeutic value, *cp.* Farbenfabriker vorm. Friedr. Bayer & Co. D. R. P. 209728.

Purine $C_5N_4H_4$,  , was prepared by Fischer (Ber. 1897, 30, 2208, 2220; 1898, 31, 2550) from uric acid by the following series of reactions: potassium urate and phosphoryl chloride at 160°–170° yield 2 : 6-*dichloro*-8-*oxypurine*, which on further treatment with excess of the chloride at 150°–155°, is converted into 2:6:8-*trichloropurine*; when this is treated with hydriodic acid and phosphonium iodide at 0° it suffers partial reduction yielding 2 : 6-*di-iodopurine*, which is completely reduced to *purine* on boiling with zinc-dust and water. The synthesis of purine has been effected by Isay (Ber. 1906, 39, 250) from nitrouracil, which is converted by phosphoryl chloride at 188° into 2 : 6-*dichloro*-5-*nitropyrimidine*; this yields 2-*chloro*-5-*nitro*-4-*aminopyrimidine* by the action of ammonia. On reduction with hydriodic acid and phosphonium iodide, 4:5-*diaminopyrimidine* is obtained. The 5-formyl derivative of this base loses water when heated above 198° yielding purine



Purine is a readily soluble crystalline compound, m.p. 216°–217° (corr.). It forms salts both with acids and bases; the *zinc* salt is very sparingly soluble; *v.* Salkowski (Zeitsch. physiol. Chem. 1913, 85, 346; Biochem. Zeitsch. 1913, 55, 254) for the precipitation of purine bases by zinc salts; *cf.* Thar (Biochem. Zeitsch. 1913, 52, 435; 56, 353); the *nitrate* $C_5N_4H_4 \cdot HNO_3$ melts and decomposes at 205°; the yellow *picrate* $C_5N_4H_4 \cdot C_6H_3N_3O_7$ melts at 208°. The base is very stable towards

oxidising agents and in consequence does not give the murexide reaction. 2 : 6 : 8-*Trichloropurine* $C_5N_4HCl_3,5H_2O$ becomes anhydrous at 110°, melts with decomposition at 187°–189° (corr.), and dissolves in 70 parts of hot water; tetra-acetyltrichloropurine-*d*-glucoside,m.p.168°–169° (corr.), has $[\alpha]_D^{20}$–26·02°, Fischer and Helferich (Ber. 1914, 47, 210). 2 : 6-*Diiodopurine* $C_5N_4H_2I_2$ melts at 224° with decomposition. 2 : 6-*Dichloro*-8-*oxypurine* $C_5N_4HCl_2O$ decomposes above 350° without melting, dissolves in 120 parts of boiling alcohol or 1000 parts of boiling water. It yields 8-*oxypurine* on reduction, m.p. 317° (corr.). 6-*Amino*-8-*oxy*-2-*chloropurine* is obtained by the action of ammonia on the dichloro compound; it carbonises above 360° without melting, and yields the base 6-*amino*-8-*oxypurine* on reduction; this is converted by nitrous acid into 6 : 8-*dioxypurine*, an isomeride of xanthine, m.p. above 400° with decomposition. 2 : 8-*dioxypurine*, also an isomeride of xanthine, gives a strong murexide reaction; its sodium salt forms stout prisms containing four molecules of water of crystallisation; the sodium salt of xanthine contains only one molecule of water, Johns (Amer. Chem. J. 1911, 45, 80).

For alkyl derivatives of the oxy- and dioxypurines *v.* Johns (J. Biol. Chem. 1911, 9, 161; *ibid.* 1912, 11, 67 and 73, and 393; *ibid.* 1912, 12, 91; *ibid.* 1913, 14, 1; 1913, 15, 119; 1913, 16, 135; *ibid.* 1914, 17, 1); Johns and Hendrix, (*ibid.* 1914, 19, 25); and for hydroxythiopurines and alkyl hydroxythiolpurines, Johns and Hogan (*ibid.* 1913, 14, 299); Johns and Baumann (*ibid.* 1913, 14, 381).

The following naturally occurring purines are described under their respective titles in other parts of this work:

Adenine, 6-*aminopurine.*
Guanine, 2-*amino*-6-*oxypurine.*
Hypoxanthine, 6-*oxypurine.*
Xanthine, 2 : 6-*dioxypurine.*
Heteroxanthine, 7-*methyl*-2 : 6-*dioxypurine.*
Paraxanthine, 1 : 7-*dimethyl*-2 : 6-*dioxypurine.*
Theophylline, 1 : 3-*dimethyl*-2 : 6-*dioxypurine.*
Theobromine, 3 : 7-*dimethyl*-2 : 6-*dioxypurine.*
Caffeine, 1 : 3 : 7-*trimethyl*-2 : 6-*dioxypurine.*
Uric acid, 2 : 6 : 8-*trioxypurine.*

M. A. W.

PURPLE, HESSIAN, *v.* AZO-COLOURING MATTERS.

PURPLE OCHRE (*Mars violet*) *v.* PIGMENTS.

PURPLE OF CASSIUS *v.* GOLD PURPLE.

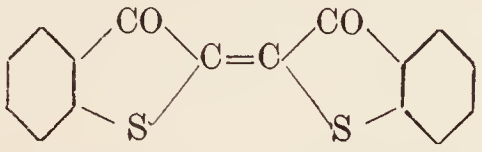
PURPLE OF MOLLUSCA *v.* PURPLE OF THE ANCIENTS; PUNICIN; INDIGO.

PURPLE OF THE ANCIENTS. The ancients derived their purple from certain molluscs or sea-snails, the *Purpura hæmastoma*, known to Pliny as *Buccinum*, and from the *Murex brandaris*, called by Pliny *Purpura*. At Athens and Pompeii, large quantities of the shells have been discovered lying in heaps close to ancient dye-works. These molluscs are to be found throughout the whole of the Mediterranean, and, indeed, in the sea in numerous parts of the world varieties exist which may be employed for dyeing purposes. Two sorts of purple, known as Tyrian and Byzantium purple, were recognised by the ancients, the former possessing a redder tint than the latter.

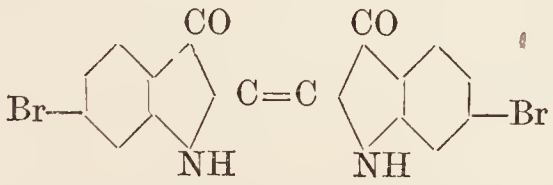
From the observations of Cole (Phil. Trans. 1685), Réaumer (Mem. de l'Acad. Royale des Sciences, 1711), and Bancroft (Philosophy of Permanent Colours, 1, 120, 1803), it appears that the colour-producing secretion, which resembles pus in appearance and consistence, is contained in a small whitish cyst or vein, placed transversely under, but in immediate contact with, the shell, and near the head of the animal. This pus-like matter, either diluted with water or undiluted, on being applied to bits of white linen or calico and exposed to sunlight rapidly changes its colour, passing from yellow, through light green, deep green, and 'watchet blue,' to purplish-red or crimson. To produce this change of colour the light of the sun is essential. It is effected more rapidly by the direct action of the sun's rays than by that of diffused light, but it does not take place in moonlight or in artificial light. If the linen or other fabric to which the secretion has been applied is kept in the dark, it remains unchanged, but when exposed to the sun it becomes purple, even after the lapse of years, though a little more slowly than at first. The metamorphosis which the change of colour indicates is not sensibly promoted by heat. It proceeds in a vacuum and in hydrogen or nitrogen gas as speedily as in air on exposure to light. The colour produced is remarkably stable, resisting the action of soap, alkalis, and most acids, being destroyed only by nitric acid and chlorine (*see* also Bizis, Journ. de Ch. Med. 1835, 10, 99, and A. and G. de Negri, Gazz. chim. ital. 1875, 437). Schunck (Chem. Soc. Trans. 1879, 35, 591), who examined the *Purpura capillus*, which he procured from the rocks at Hastings, finds that the colouring matter (punicin) is quite insoluble in water, alcohol, or ether, sparingly soluble in boiling benzene or boiling glacial acetic acid, and readily soluble in boiling aniline, giving a solution which is at first green, but as it approaches saturation becomes purplish-blue. At this point it shows a broad, well-defined absorption band, beginning near C and extending beyond D; but as the solution cools, depositing the substance contained in it, the colour changes to green, and the band becomes gradually narrower, until it occupies the space midway between C and D, and then disappears. The masses of colouring matter deposited from the solution in aniline are seen, under the microscope, to consist of star-shaped groups of irregular crystalline needles, which, when very thin, show by transmitted light a purple colour. Punicin is soluble in oil of vitriol, giving a dirty purple colour, and showing a broad ill-defined absorption-band between D and E, the green and blue of the spectrum being much darkened. On heating the solution slightly, or allowing it to stand for some time, the colour changes to a bright bluish-green and it now shows an absorption-band in the red. Punicin is also sparingly dissolved by a hot alkaline solution of stannous oxide, and the solution on exposure to air becomes covered with a blue pellicle. Punicin may be sublimed, giving crystals which show by reflected light a semi-metallic lustre, like that of sublimed indigo-blue (Schunck, *l.c.*). Witt (Technologie der Gespinnstfasern, 1888) expressed the opinion that the colouring matter yielded by these molluscs was an admixture of

indigotin with a red colouring matter not so fast to light.

Friedländer (Annalen, 351, 390; Ber. 1906, 39, 1060) examined the dye yielded by the *Murex brandaris* and *Murex trunculus* which he obtained from the zoological station at Trieste. Letellier (Compt. rend. 1891, 109, 82) had observed that, in addition to the colouring principle, organic sulphur compounds were also present in these glands, and it suggested itself, therefore, to Friedländer as possible that the 'purple of the ancients' might in reality consist of thioindigotin



To isolate the colouring matter the glands of the molluscs were spread out as thinly as possible upon filter paper, which was then exposed to the sunlight for half an hour. The highly coloured product was now immersed in diluted hydrochloric acid (1 : 1), the mixture evaporated to dryness on the water-bath, the residue extracted with hot water, and washed with alcohol and ether. In this manner a product consisting only of cellulose and the pure colouring matter was obtained, and the latter could be readily removed by extraction with boiling anisole, from which it separates in the crystalline condition. Finally, it was recrystallised from nitrobenzene. It consists of dark violet crystals which possess a coppery lustre, dissolves in hot, high-boiling solvents with a blue-violet colour, yields a sublimate on heating, and in mumerous respects resembles the colouring matter of the indigo group. Analysis indicated the absence of sulphur, although nitrogen was found to be present. The absorption spectrum is similar to that given by indigotin; but, on the other hand, it is distinguished from this latter colouring matter by its sparing solubility, and by giving with cold concentrated sulphuric acid a reddish-violet coloration. With fuming sulphuric acid it yields a soluble blue sulphonic acid, and when reduced in alkaline solution forms a pale yellow liquid, from which, when exposed to air, it separates as a reddish-violet precipitate. In a later paper by the same author (Ber. 1909, 42, 765) some slight modifications of the method for the isolation of the dye from the *Murex brandaris* are given, and it is shown that in this manner about 12,000 molluscs are required for the preparation of 1·4 grms. of the substance. This colouring matter contains bromine, and by a comparison with the synthetic dye there can be no doubt that it is in reality 6 : 6′-dibromoindigotin.

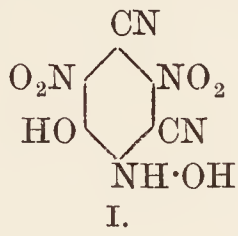


Further investigation has indicated that in addition to this dibromindigotin another dye of a bluer shade also containing bromine, but possessing a greater solubility in organic solvents, is produced from the *Murex brandaris*. It contains more carbon and less bromine than dibromindigotin, but its constitution is as yet undetermined (Friedländer, Chem. Zeit. 1911, 640). The dyes obtained from *Purpura aperta* and from *P. lapillus*, according to Friedländer (Ber. 1922, 55 [B] 1655) appear to be identical with 6 : 6′-dibromoindigotin. A. G. P.

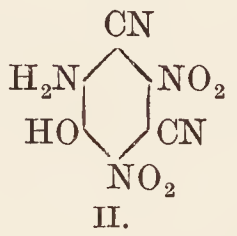
PURPURIC ACID *v.* MUREXIDE.

*iso***PURPURIC ACID.** When picric acid is added to a solution of potassium cyanide, the mixture becomes reddish-brown, and finally purple. Hlasiwetz (Annalen, 1859, 110, 289) first isolated the coloured compound and found it to be the potassium salt of an acid which he considered was isomeric with purpuric acid; he therefore gave it the name of iso*purpuric acid*, and prepared the ammonium, calcium, barium, lead, and silver salts by double decomposition (compare also Baeyer, J. 1858, 458). The potassium salt was formerly employed as a dye under the name *Grenat Brown*.

The *iso*purpurates are decomposed by the action of dilute nitric, sulphuric, or hydrochloric acid, but the free *iso*purpuric acid has been isolated from the ammonium salt by treating it with one equivalent of phosphoric acid at 0°; it is dark violet, and readily decomposed even by dissolving in water or in the ordinary organic solvents (Borsche and Böcker, Ber. 1904, 37, 4388). According to Borsche, the constitution of *iso*-purpuric acid is 2 : 4-dicyano-3 : 5-dinitro-6-hydroxy-β-phenylhydroxylamine I. (Ber.1900, 33, 2719, 2995); but Nietzki and Petri (*ibid.* 1900, 33, 1788) regard it as an amino compound of the constitution 5-hydroxy-6-amino-2 : 4-dinitro*iso*phthalonitrile II.



I.



II.

Fierz and Brütsch (Helv. Chim. Acta, 1921, 4, 375) regard *iso*purpuric acid as 4 : 6-dinitro-*l*-hydroxy-2-hydroxylamino-3 : 5 dicyanobenzene.

The development of the characteristic colour of *iso*purpuric acid when picric acid is mixed with an alkali cyanide is commonly used as a test for cyanides. Reichard (Chem. Zeit. 1901, 25, 537) finds that 1 part of potassium cyanide in 2000 parts of water can be thus detected, although the development of the colour requires 24 hours; he also finds that the metallic cyanides, other than those of the alkalis, do not form purpurates with picric acid.

Test for cyanogenetic glucosides. Guignard (Compt. rend. 1906, 142, 545) has used the reaction as a delicate test for the presence of prussic acid among the products of hydrolysis of substances containing cyanogenetic glucosides. Using test-papers prepared from sodium picrate, exposed to the action of the gaseous products of hydrolysis of the material under investigation, the presence of 0·00005 grm. of prussic acid can be detected after 12 hours', and 0·00002 grm. after 24 hours' exposure.

*meta***Purpuric acid.** Potassium cyanide forms purple compounds when added to a nitrophenol containing at least two nitro groups in the molecule, which must be in the *meta* position to one another, and at least one of them *ortho* to

the hydroxyl group. The compound formed by the interaction of potassium cyanide and 2 : 4-dinitrophenol is the salt of *metapurpuric acid*, and is the *potassium salt of* 4-*nitro*-2-*hydroxylamino*-3-*cyanophenol*, it forms dark red needles, fairly readily soluble in water or acetic acid, sparingly so in acetone or alcohol, melts and decomposes above 250°, and yields barium, strontium, copper, and silver salts by double decomposition. It is oxidised by the action of dilute nitric acid or potassium hypobromite yielding 2 : 6-dinitro-3-hydroxybenzonitrile. *meta*Purpuric acid can be prepared from the ammonium salt by treating it with one equivalent of phosphoric acid in aqueous solution at 0° ; it is a dark red powder, decomposes at 92°, yielding nitric oxide (Pfaundler and Oppenheim, Zeitsch. Chem. 1865, 470 ; Sommaruga, Annalen, 1871, 157, 335 ; Borsche, Ber. 1900, 33, 2718, 2723 ; Borsche and Böcker, *ibid.* 1903, 36, 4357 ; 1904, 37, 1843, 4388 ; Borsche and Gahrtz, *ibid.* 1905, 38, 3538 ; 1906, 39, 3359 ; Borsche and Heyde, *ibid.* 1905, 38, 3938).

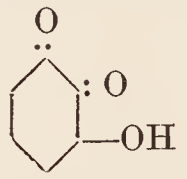
PURPURIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

PURPUROGALLIN $C_{12}H_8O_5$. By treating pyrogallol in acid solution with silver nitrate or potassium permanganate, A. Girard (Ber. 1869, 2, 562) obtained a red substance $C_{20}H_{16}O_9$, which he named purpurogallin. A. Wichelhaus (Ber. 1872, 5, 848), by oxidising pyrogallol with quinone, obtained the same substance (pyrogallol quinone), and gave it the formula $C_{18}H_{14}O_9$ and the constitution $(OH)C_6H_3[O{\cdot}O{\cdot}C_6H_3(OH)_2]_2$. Struve (Annalen, 1872, 163, 102) made the interesting discovery that purpurogallin is formed by allowing a mixture of pyrogallol and gum arabic solutions to stand in contact with air for some hours. On repeating these experiments, Clermont and Chautard (J. 1882, 682) succeeded in obtaining a yield of 67 p.c. of purpurogallin by the gum arabic method. These authors also employed platinum black as oxidising agent, and observed the production of carbon dioxide during the formation of purpurogallin ; they describe a tetra-acetyl derivative $C_{20}H_{12}O_9(C_2H_3O)_4$, m.p. 186°, sodium and barium salts $C_{20}H_{12}Na_4O_9$, $C_{20}H_{12}Ba_2O_9$, and a tetrabromo compound $C_{20}H_{12}Br_4O_9$, m.p. 202°–204°. Heated with sulphuric acid, purpurogallin gave the compound $C_{20}H_{12}O_{10}$, and by means of hydriodic acid a mixture of hydrocarbons $(C_{10}H_{14})_n$ was formed. S. Hooker (Ber. 1887, 20, 3259) employed potassium ferricyanide as the oxidising agent, the yield being 13 to 14 p.c., and also prepared purpurogallin by the action of potassium nitrite on a solution of gallic acid in the cold. Nietzki and Steinmann (*ibid.* 1887, 20, 1277) obtained the best yields of purpurogallin by treating a well-cooled aqueous solution of pyrogallol acidified with acetic acid, with sodium nitrite, and were indebted for this method to a private communication from Nölting. As by distillation with zinc-dust purpurogallin was found to yield naphthalene, it seemed evident that such a nucleus pre-exists in this compound, and it was considered likely that during the oxidation of the pyrogallol some of the benzene nuclei are split up, and that condensation of the product ensues to form this naphthalene ring. Acetyl purpurogallin was again examined, and the formula $C_{20}H_{16}O_9$ considered as probably representing the colouring matter itself.

Perkin and Steven (Chem. Soc. Trans. 1903, 83, 192) obtained from pyrogallol by means of potassium ferricyanide (Hooker, *l.c.*) only 14 p.c. of purpurogallin, whereas the nitrous acid method (Nietzki and Steinmann) gave from 20 to 32·5 p.c. In the latter case, 20 grms. of pyrogallol dissolved in 300 c.c. of water were treated with 8 c.c. of glacial acetic acid, the solution cooled by addition of ice, and slowly treated with 8 grms. of sodium nitrite shaking well after each addition. The precipitate of purpurogallin was removed after an hour, and the filtrate allowed to stand overnight, as frequently a further quantity of the colouring matter then separated.

A. G. Perkin and F. M. Perkin (Chem. Soc. Trans. 1904, 85, 243) obtained purpurogallin by the electrolytic oxidation of pyrogallol in the presence of a 15 p.c. solution of sodium sulphate, employing a rotating anode. Satisfactory results were also obtained when, instead of rotating the anode, a rapid stream of air was blown through the mixture, the yield thus averaging from 36·4 to 37 p.c.

When pyrogallol in alcoholic solution is treated with acetic acid and *iso*amyl nitrite, it gives a compound $C_6H_4O_3$ or $C_{12}H_8O_6$, colourless prismatic needles, m.p. 206°–208°, in minute amount, the acetyl derivative of which melts at 283°–285° (P. and S. Chem. Soc. Trans. 1906, 89, 802). As on reduction with zinc-dust and acetic acid pyrogallol is regenerated, it is possible that this substance is hydroxy-*o*-benzoquinone



Digested with boiling water, purpurogallin, a soluble compound $C_{12}H_{10}O_7$(?), m.p. 242°–243°, and a brown resin are produced, and this result renders it not improbable that the compound $C_6H_4O_3$ represents an intermediate stage in the formation of purpurogallin from pyrogallol by the ordinary methods. Wichelhaus (*l.c.*), indeed, predicted that the first product of the oxidation of pyrogallol by his methods is a hydroxy-quinone.

Ruzicka (Monatsh. 1910, 31, 799), who experimented with the gum arabic method of Clermont and Chautard (*l.c.*), could obtain only a 24 p.c. yield of purpurogallin in this manner.

Perkin and Steven, as the result of cryoscopic determinations, consider that the molecular weight of purpurogallin is best expressed by the formula $C_{11}H_8O_5$, and show that the acetyl and bromine derivatives described by Clermont and Chautard should be respectively represented as $C_{11}H_4O_5(C_2H_3O)_4$ and $C_{11}H_6Br_2O_5$.

When purpurogallin is methylated by means of methyl iodide *purpurogallin trimethyl ether* $C_{11}H_5O_2(OCH_3)_3$, orange-yellow needles, m.p. 174°–177°, which yields the acetyl derivative $C_{11}H_4O_2(OCH_3)_3C_2H_3O$, colourless needles, m.p. 140°–143°, is produced. A considerably better yield can be obtained by the employment of methyl sulphate (Perkin, Chem. Soc. Trans. 1912, 101, 803), whereas, according to Ruzicka (*l.c.*), diazomethane quantitatively converts purpurogallin into the trimethyl compound. Digested

with alcoholic potash at 170°, purpurogallin trimethyl ether gives a small quantity of an acid $C_{13}H_{12}O_5$ (P. and S.), $C_{11}H_6O_3(OCH_3)_2$ (R.), m.p. 197°–199° (Chem. Soc. Proc. 1905, 21, 211), which is in reality *purpurogallone dimethyl ether*. Strongly heated, it yields a sublimate which is an anhydride, m.p. 164°–166°, and the same compound is formed with boiling acetic anhydride.

By the action of methyl sulphate and alkali on the trimethyl compound *purpurogallin-tetramethyl ether* $C_{11}H_4O(OCH_3)_4$, prisms, m.p. 93°–95° (P.), 91°–92° (R.), is produced, and from this, by means of alcoholic potash at 170°, a small amount of an acid can be obtained.

When purpurogallin is digested with 50 p.c. aqueous potassium hydroxide at about 170°, iso*purpurogallone* $C_{22}H_{16}O_{10}$, yellow prismatic needles (m.p. above 300°), and *purpurogallone* $C_{11}H_8O_5$, m.p. 262°–264°, are obtained. Distilled with zinc-dust the latter compound gives naphthalene, and when digested with hydriodic acid (sp.gr. 1·7) among other substances *β-naphthol* and 2 : 3-*dihydroxynaphthalene* are produced (Chem. Soc. Trans. 1912, 101, 803). Sulphuric acid converts *iso*purpurogallone into *anhydro*-iso-*purpurogallone* $C_{22}H_{10}O_8$, yellow prisms (m.p. above 310°), and with acetic anhydride *acetyl-anhydro* - iso*purpurogallone* $C_{22}H_8O_8(C_2H_3O)_4$, colourless needles, m.p. 280°–282°, is produced. iso*Purpurogallone tetramethyl ether*, colourless needles, m.p. 211°–213°, can be prepared by means of methylsulphate. Whereas purpurogallone is a trihydroxynaphthalene carboxylic acid, *iso*purpurogallone is the corresponding dinaphthyl compound (*l.c.* 1912).

Purpurogallin carboxylic acid $C_{11}H_7O_5{\cdot}COOH$, orange-red needles (m.p. above 330°), is obtained in small quantity by oxidising gallic acid in aqueous solution with potassium ferricyanide in the presence of potassium or sodium acetate. Much larger amounts are, however, produced by the electrolytic oxidation of gallic acid (A. G. and F. M. Perkin, Chem. Soc. Trans. 1908, 98, 1186) employing sodium sulphate (yield 34 p.c.) or sodium acetate (yield 30–40 p.c.) as electrolytes. *Sodium purpurogallin carboxylate*

$$C_{12}H_7O_7Na,4H_2O$$

orange-brown leaflets; *potassium purpurogallin carboxylate* $C_{12}H_7O_7K,3H_2O$, orange-red prismatic needles; and *barium purpurogallin carboxylate* $(C_{12}H_7O_7)_2Ba$, needles; *methylpurpurogallin carboxylate tetramethyl ether*

$$C_{11}H_3O(OME)_4CO_2Me$$

colourless needles, m.p. 120°–121°; and *purpurogallin carboxylic acid tetramethylether*

$$C_{11}H_3O(OMe)_4COOH$$

needles, m.p. 182°–183°, have been prepared.

Boiling aqueous potassium hydroxide (50 p.c.) converts purpurogallin carboxylic acid into *purpurogallone carboxylic acid* $C_{12}H_8O_7,2H_2O$ yellow needles (m.p. above 300°), which gives *acetyl-anhydro-purpurogallone carboxylic acid*

$$C_{12}H_4O_6(C_2H_3O)_2$$

colourless needles, m.p. 236°–238°; *methyl-purpurogallone carboxylate tetramethyl ether* $C_{11}H_3O(OMe)_4CO_2Me$, colourless prisms, m.p. 110°–111°; and *purpurogallone carboxylic acid tetramethyl ether* $C_{11}H_3O(OMe)_4COOH$, needles, m.p. 166°–167°.

Purpurogallin and purpurogallin carboxylic acid are powerful dyestuffs, whereas the purpurogallones and purpurogallone carboxylic acid possess a similar property, although in a less marked degree. On mordanted wool the following shades are produced:—

	Chromium	*Aluminium*	*Tin*	*Iron*
Purpurogallin	Reddish chocolate brown	Brownish red	Brick red	Deep black
Purpurogallin carboxylic acid	Reddish brown	Reddish puce	Brick red	Brownish black
Purpurogallones	Chocolate brown	Pale chocolate brown	Pale yellow	Chocolate brown
Purpurogallone carboxylic acid				

The fact that purpurogallin on distillation with zinc-dust gives naphthalene suggests that this colouring matter is a β-naphthoquinone derivative, in which, owing to the ready oxidisability of its alkaline solution, a pyrogallol nucleus is present. On the other hand, its exact structure has not yet been determined.

A. G. P.

PURPUROXANTHIN 1 : 3 - *Dioxyanthraquinone v.* ALIZARIN AND ALLIED COLOURING MATTERS.

PURREE, PIURI, or **PIOURY,** *v.* INDIAN YELLOW.

PUTREFACTION *v.* FERMENTATION.

PUTREFACTION BASES (Ptomaines). As early as 1856, Panum found that a toxic substance, which was not destroyed by boiling and had physiological effects similar to curare, was present in certain septic fluids. Dupré and Bence-Jones (Zeitsch. Chem. Pharm. 1866) extracted a substance from the animal body which gave the reactions of an alkaloid, and a blue fluorescence in sulphuric acid solution, and which they called 'animal quinoidine.' About the same time Marquardt described an alkaloidal substance 'septicine,' which he obtained from a corpse, and which gave reactions similar to coniine. Among other workers were Schmidt, and Bergmann and Schmiedeberg, who described a toxic crystalline substance 'sepsin,' which, when injected into the body, produced symptoms of septicæmia; Zuelzer and Sonnenschein (1869), who obtained a very small quantity of a substance resembling atropine in its physiological action. Selmi, in the course of the medicolegal examination of human corpses, obtained in 1870 and 1871 bases giving alkaloidal reactions, which he was unable to identify with any known vegetable alkaloid, and for which he suggested the name *ptomaines* (πτῶμα, corpse). This term was adopted by Gautier for bases formed in the putrefaction of proteins, and was later applied to products of bacterial metabolism in general by Brieger, Griffiths, and others. There is very little evidence that what is now popularly called 'ptomaine poisoning' is due to poisonous bases. None of the putrefaction bases which have been properly investigated have a physiological action that could explain the symptoms of 'ptomaine poisoning'; the latter is most frequently due to bacterial infections (*Bacillus botulinus*, Gaertner's bacillus). Examples of relatively simple substances alleged to have the properties of poisonous food are *tyrotoxicon* from cheese (Vaughan, Zeitsch. physiol. Chem. 1886, 10, 146), *mytilotoxine* $C_6H_{15}O_2N$ from poisonous mussels (Brieger, Die Ptomaine, I–III., 1885, 1886), and *sepsine* $C_5H_{14}O_2N_2$

from putrid yeast (Faust, Arch. exp. Path. Pharm. 1904, 51, 248). The formulæ of all three are still doubtful. The bacterial toxins, which are very much more complex, may be very poisonous, *e.g.* that of *B. botulinus*, which is readily destroyed at 80° and yields an antitoxin (Van Ermengem, Zeit. f. Hyg. Infekts. 1897, 26, 1; *also* in Kolle und Wassermann's Handbuch der pathogenen Mikro-organismen, 1912, iv. 909).

The term ptomaine has now fallen into disuse in scientific literature; instead we may employ the term *putrefaction bases* to describe bases resulting with breakdown of proteins and lipoids by bacterial action, and with our knowledge of the structure of the starting material, so also our knowledge of putrefaction bases has in recent decades been placed on a sure foundation. Bacteria appear first to break down proteins to the constituent amino-acids, and these may be broken down further either by elimination of ammonia (deaminisation) or by elimination of carbon dioxide (decarboxylation). In the latter case putrefaction bases result, and the bases corresponding to nearly all the 18 or 19 known amino acids of protein have been isolated and studied. The first of these to be obtained, *phenylethylamine*

$$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$$

(Nencki, 1876) was considered to be identical with collidine from bone oil; Nencki later correctly identified it and surmised its origin from the amino-acid phenylalanine

$$C_6H_5{\cdot}CH_2CH(NH_2)COOH$$

It so happens that phenylethylamine is one of the few bases of this class which can conveniently be isolated by the Stas-Otto process in use for vegetable alkaloids (*see* art. Alkaloids). Generally putrefaction bases cannot be removed from alkaline aqueous solution by shaking with chloroform or other solvents, but have to be precipitated as phosphotungstates, mercuri-, platini-, or aurichlorides or other compounds, little soluble in water; this method was first developed by Brieger, and led him to the discovery of *putrescine* (tetramethylene diamine) and *cadaverine* (pentamethylene diamine) derived from ornithine and lysine respectively, by decarboxylation, as was first proved by Ellinger (Zeitsch. physiol. Chem. 1900, 29, 334). Both bases have often been isolated from putrified material, and also from fungi, and from the urine in cystinuria (Udranszky and Baumann, *ibid.* 1889, 13, 562).

Iso*butylamine* $C_4H_9{\cdot}NH_2$, is formed from valine (Neuberg and Karczag, Biochem. Zeitsch. 1909, 18, 435) and *isoamylamine*, $C_5H_{11}{\cdot}NH_2$, from leucine (Barger and Walpole, J. Physiol. 1909, 38, 343); the latter base can, like phenylethylamine, be extracted with chloroform from aqueous solution.

p-*Hydroxyphenylethylamine* or *tyramine*

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$$

from tyrosine may be extracted with amyl alcohol from a sodium carbonate but not from a caustic soda solution (Barger and Walpole), and is then best converted into the dibenzoyl derivative, m.p. 170°. In this way it may be readily isolated from cheese. The decarboxylation of tyrosine may be most readily effected by heating in a good vacuum to 260°–270° (yield 50 p.c.; F. Ehrlich and Pistschimuka, Ber. 1912, 45, 1006).

Indolethylamine, 3-*β*-*aminoethylindole*, $C_{10}H_{12}N_2$, was obtained in the putrefaction of tryptophane by Laidlaw (Biochem. J. 1911, 6, 141), and synthetically by Ewins (Chem. Soc. Trans. 1911, 99, 270).

β-Iminazolylethylamine (*histamine*, 4-*β*-*amino-ethylglyoxaline*) $C_5H_9N_3$, was first obtained in quantity by the putrefactive decarboxylation of histidine (Ackermann, Zeitsch. physiol. Chem. 1910, 64, 504), although it had already been synthesised on a small scale by Windaus and Vogt (Ber. 1907, 40, 3691). A still complicated synthesis by Pyman (Trans. Chem. Soc. 1911, 99, 668) has been applied technically. Histidine can scarcely be decarboxylated by heat alone, but with 20 p.c. sulphuric acid at 265°–270° in sealed tube Ewins and Pyman (Trans. Chem. Soc. 1911, 99, 339) obtained a 25 p.c. yield of the histamine. The putrefactive decarboxylation has been patented and used industrially (D. R. P. 250110 of F. Bayer & Co.; D. R. PP. 252872, 252873, 252874, 256116 of Hoffmann, La Roche & Co.; compare *also* Ackermann (*l.c.*); Mellanby and Twort, J. Physiol. 1912, 45, 53; and Berthelot and Bertrand, Compt. rend. 1912, 154, 1643, 1826). Without suitable cultures and conditions of growth the yield is rather uncertain; possibly a better method is to convert histidine, according to Dakin (Bio-Chem. J. 1916, 10, 319), by means of sodium p-toluene sulphochloroamide (chloramine–T) into cyanomethylglyoxaline (80 p.c. yield) and reduce this nitrile with sodium and alcohol to histamine, as in Pyman's synthesis (*l.c.*).

The four last-mentioned bases and phenylethylamine are all physiologically active; isoamylamine, tyramine and histamine have been isolated from ergot extracts (*see* Ergot). Under certain conditions small doses of histamine may produce very powerful effects which have been much studied of late, but none of these bases produce the symptoms of ptomaine poisoning.

The bacterial desamination of diamino acids may result in the formation of putrefaction bases containing a carboxyl group, *e.g.* *δ-amino*-n-*valeric acid* $NH_2(CH_2)_4COOH$, from ornithine or arginine (E. and H. Salkowski, Ber. 1883, 16, 1191; Ackermann, Zeitsch. physiol. Chem. 1907, 54, 1), *iminazolylpropionic acid*

$$C_6H_8O_2N_2$$

(Ackermann, *ibid.* 1910, 64, 504), and *iminazolylacrylic* or *urocanic acid* $C_6H_6O_2N_2$ (Raistrick, Bio-Chem. J. 1917, 11, 71), both from histidine.

β-Alanine $NH_2(CH_2)_2COOH$, and *γ-aminobutyric acid* $NH_2(CH_2)_3COOH$, are likewise putrefaction bases with a carboxyl group, but are formed by partial decarboxylation of aspartic and glutamic acids respectively (Ackermann, Zeitsch. Biol. 1911, 56, 87; Zeitsch. physiol. Chem. 1910, 69, 273).

All the above bases are derived from proteins. From phosphatides, *e.g.* lecithin, bacteria first set free *choline* (*q.v.*), and then apparently form *neurine*, *trimethylamine*, and *monomethylamine*. *Neurine*, *vinyltrimethyl ammonium hydroxide*, $Me_3{:}N(OH)CH{:}CH_2$, was isolated by Brieger (*l.c.*) from putrid meat and has also been found in meat extract and the suprarenal

gland; its formation from choline has never been rigorously proved. It may be prepared by the action of freshly-precipitated silver oxide on a concentrated aqueous solution of trimethyl-β-bromo-ethyl ammonium bromide and isolated as the colourless crystalline trihydrate (Meyer and Hopff, Ber. 1921, 54, (B), 2274). It is a fairly strong poison, similar to, but 10–20 times as powerful as, choline.

Trimethylamine Me_3N, certainly results from choline, and is one of the best known of putrefaction bases; it was discovered in herring brine by Winckler in 1855. *Dimethylamine* has also been found in putrid fish. *Monomethylamine* is formed in small quantity by *B. prodigiosum* from choline (Ackermann and Schütze, Arch. f. Hygiene, 1911, 73, 145; compare *also* Hasebroek, Zeitsch. physiol. Chem. 1887, 12, 148).

The last three putrefaction bases are, of course, best isolated by steam distillation. Propylamine has been reported, but was probably confused with trimethylamine, and ethylamine is also a doubtful putrefaction base. Monomethyl-, dimethyl-, ethyl-, and propylamine might result from decarboxylation of glycine, sarcosine (from creatine), alanine, and γ-aminobutyric acid respectively.

Methylguanidine $NH_2C(:NH)\cdot NH\cdot CH_3$, was isolated by Brieger from putrid horse meat, and is distinctly poisonous. Some investigators have alleged that it is a normal constituent of muscle, others that it is only formed from creatine by bacterial action. It is readily obtainable by the oxidation of creatine, and may perhaps only be formed from it by the mercury or silver salts used in its isolation.

All the above putrefaction bases have been thoroughly investigated; their constitutions, and the substances from which they are derived, are all known. In addition a number of other bases have been described, of doubtful constitution, *e.g. viridinine* $C_8H_{12}O_3N_2$, *marcitine* $C_8H_{19}N_3$, and *putrine* $C_{11}H_{26}O_3N_2$, all from putrid pancreas (Ackermann, Zeitsch. physiol. Chem. 1907, 54, 204; 1908, 57, 28). *Neuridine*, *saprine*, and *gerontine* (Breiger) are all probably identical with cadaverine

Tetanine $C_{13}H_{30}O_4N_2$, and *tetanotoxine* $C_5H_{11}N$, were obtained by Brieger from tetanus cultures, and *typhotoxine* $C_7H_{17}O_2N$, from typhoid cultures. Brieger found a base isomeric with the last named in putrid horse meat, and *mytilotoxine* $C_6H_{15}O_2N$, in poisonous mussels. Of these little-known bases we may single out *sepsine* $C_5H_{14}O_2N_2$ (?), on account of its physiological action. It was obtained by Faust (Arch. exp. Path. Pharm. 1904, 51, 248) in minute quantity from putrid yeast, and caused on intravenous injection into dogs vomiting, diarrhœa, coma, and death, symptoms somewhat resembling those of 'ptomaine poisoning.' On repeated evaporation of the aqueous solution of the sulphate, the latter is stated to be transformed to cadaverine sulphate with loss of oxygen, a very peculiar reaction.

A more detailed account of methods for isolating putrefaction bases will be found in an article by D. Ackermann, 'Die Isolierung der Faülnisbasen,' in Abderhalden's Handbuch der biochemischen Arbeitsmethoden, 1910, ii. 1002–1043. Ackermann's papers, mostly quoted above, may also be consulted, as well as the articles on Bases by P. Rona, in Abderhalden's Biochemisches Handlexicon, 1911, iv., particularly 801–827, and by G. Barger in Allen's Commercial Organic Analysis, 4th ed., 1913, vii. 341–355.

A full chemical account of the better-known bases and a brief description of the physiological properties of tyramine, histamine, &c., is found in the Simpler Natural Bases, 1914, by G. Barger, in Longman's Series of Biochemical Monographs, and in Die Biogenen Amine, by M. Guggenheim (Berlin, 1920). G. B.

PUTTY POWDER. *Stannic oxide.* Common qualities of putty powder are produced by skimming the surface of boiling tin, the scum so obtained being then freed from foreign matter and well washed and ground. The better kinds are obtained by treating tin with nitric acid, thus forming stannic oxide. It is used in enamelling to give an opaque white colour: it is also employed for polishing. *V.* TIN SALTS AND OXIDES.

PUZZUOLANA *v.* CEMENTS.

PYKNOMETER *v.* SPECIFIC GRAVITY.

PYOKTANIN. Trade name for methyl violet.

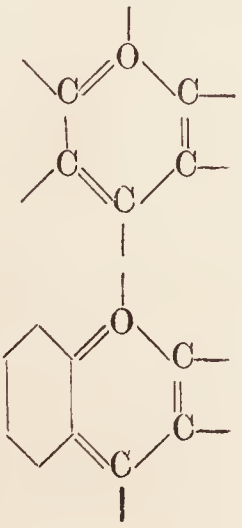
PYRACETOSALYL. Trade name for an addition product of antipyrine and acetyl salicylic acid.

PYRAMIDONE, PYRAZOLONE. The presence of pyramidone in antipyrine may be detected by adding to a hydrochloric acid solution a few drops of an acid solution of potassium ferricyanide and ferric chloride when Prussian blue is formed. With antipyrine a blood-red colour is produced changing to pale yellow (Palet, J. Soc. Chem. Ind. 1919, 54 A.). *V.* AMIDOPYYINE; SYNTHETIC DRUGS.

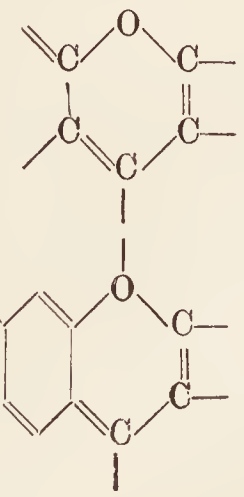
γ-PYRAN or BENZOPYRANOL GROUP.

γ-PYRAN OR BENZOPYRANOL GROUP.

The groups,



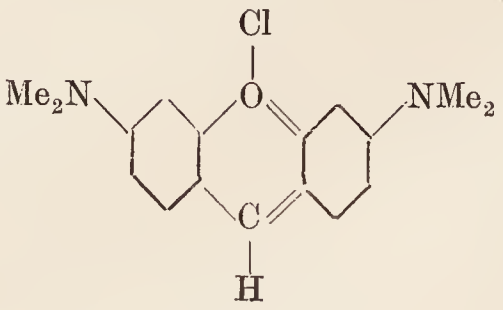
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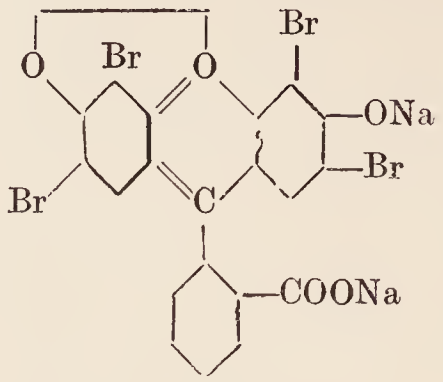
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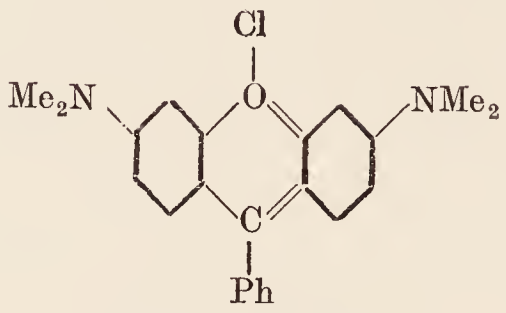
are of considerable interest in connection with both the artificial and naturally occurring colouring matters. They form the basis of a number of synthetic colours that have been in commercial use for many years, of which the following may be cited as typical instances:—



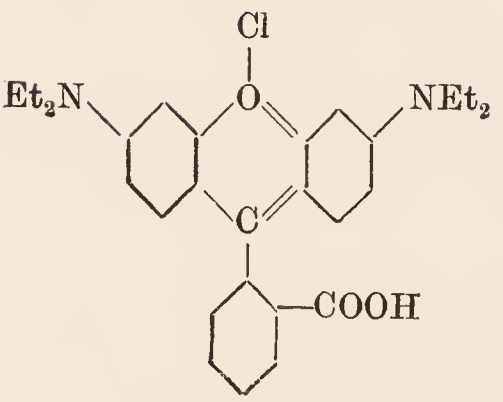
Pyronin G.



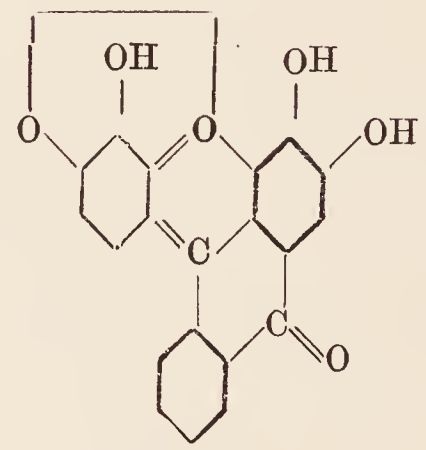
Eosin A.



Tetramethylrosamine.



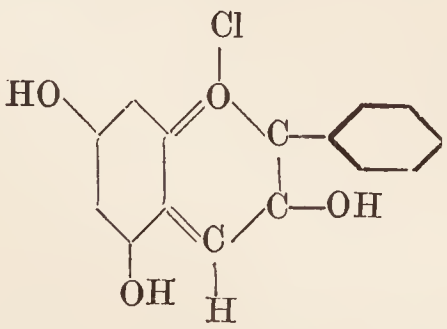
Rhodamine B.



Coerulein.

whilst related to these, but of less value, are such products as the succineins and saccharеins.

The result of researches upon naturally occurring colouring matters has been to show that a large number of substances, the *anthocyans*, colours of great beauty and widely distributed in nature, are derivatives of the benzopyranol complex; indeed all the products of this group as yet investigated are derived from the following nucleus—



by the introduction of further hydroxyl groups.

Interest in this type of compound is increased by the fact that compounds related to the anthocyans have been synthetically prepared which have rather more useful tinctorial properties than those possessed by the natural colours, and it is not impossible that the number of commercially useful derivatives in which the γ-pyran nucleus is present may be further increased. A. G. P.

PYRANTHRENE *v.* INDANTHRENE.

PYRANTIN. Trade name for *p*-ethoxyphenyl-succinimide $[CH_2{\cdot}CO]_2N{\cdot}C_6H_4{\cdot}OC_2H_5$, prepared by fusing the hydrochloride of *p*-aminophenetole or phenacetin with succinic acid. Forms colourless prismatic needles, m.p. 155.° Used as a febrifuge (Piutti, J. Pharm. Chim. 16, 298). *V.* SYNTHETIC DRUGS.

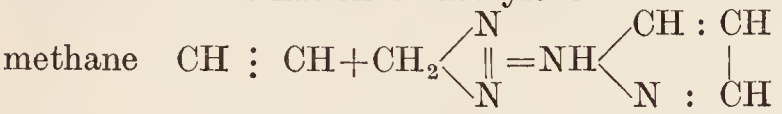
PYRARGYRITE, or dark-red silver ore (Ger. *Dunkles Rothgiltigerz*; Span. *Rosicler obscuro*). Silver sulphantimonite, Ag_3SbS_3, crystallised in the rhombohedral system. Well-formed crystals are not uncommon; these are black with a metallic-adamantine lustre, but thin splinters are translucent and dark red. The purplish-red streak serves to distinguish pyrargyrite from the closely allied mineral proustite (*q.v.*). Hardness, $2\frac{1}{2}$, sp.gr. 5·85. It occurs in metalliferous veins, and is occasionally found in sufficient amount to be of importance as an ore of silver (Ag 59·9 p.c.); *e.g.* formerly at Andreasberg in the Harz mountains; at Guanajuato in Mexico; and at Colquechaca in Bolivia.

L. J. S.

PYRAZINE *v.* AZINES.

PYRAZOLE $C_3H_4N_2$ has the structural formula (1) NH<(5) CH : CH(4) / (2) N : CH(3)>, the orientation of radicles within the ring being designated by the

numbers as shown. It is isomeric with glyoxaline or iminazole, and is sometimes termed *α*-pyrazole to distinguish it from its isomerides, which are known as *β*-pyrazoles. Pyrazole has been prepared by a variety of methods: thus by the direct combination of acetylene and diazomethane



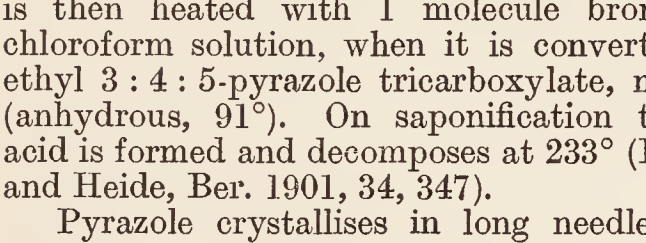
(Pechmann, Ber. 1898, 31, 2950); by the condensation of epichlorhydrin with hydrazine hydrate in presence of zinc chloride (Balbiano, *ibid.* 1890, 23, 1105); by the oxidation of a chloroform solution of pyrazoline with bromine (Curtius and Wirsing, J. pr. Chem. 1894, [ii.] 50, 544); but it is, perhaps, most conveniently prepared by heating pyrazole di- or tri-carboxylic acid or its ester to 230°–240°. The latter is itself readily obtained from ethyl diazoacetate by heating it with dimethyl acrylic ester for two hours on a water-bath. The purified 3 : 4 : 5-pyrazoline tricarboxylic ester so obtained is then heated with 1 molecule bromine in chloroform solution, when it is converted into ethyl 3 : 4 : 5-pyrazole tricarboxylate, m.p. 71° (anhydrous, 91°). On saponification the free acid is formed and decomposes at 233° (Buchner and Heide, Ber. 1901, 34, 347).

Pyrazole crystallises in long needles, m.p. 70°, b.p. 187°, and is readily soluble in water. It is more stable and basic in character than pyrrole, and it has the general properties of an aromatic substance (Knorr, *ibid.* 1895, 28, 715). It also resembles pyridine in its double salts with a number of metallic chlorides and sulphates, and in the properties of its alkyl derivatives. It forms salts with the halogen, sulphuric, and picric acids (Buchner and Fritsch, Annalen, 1893, 273, 257; Mandalà, Gazz. chim. ital. 1910, 40, i. 117). When reduced it forms pyrazoline.

Treated with fuming sulphuric acid it yields a *sulphonate* (Eppler, Zeitsch. Krist. 1898, 29, 233). *Halogen* (Knorr, *l.c.*; Ber. 1904, 37, 350; Buchner and Fritsch, *l.c.*; Mazzara and Borgo, Atti R. Accad. Lincei, 1906, [v.] 15, i. 704), *nitro* (Hell and Torrey, Amer. Chem. J. 1899, 22, 105; Buchner, Annalen, 1893, 273, 217; Knorr, *ibid.* 1894, 279, 278), *amino* (Knorr, Ber. 1895, 28, 715), and *nitro halogen* (Black and Hill, Amer. Chem. J. 1905, 33, 292) derivatives have been obtained.

Pyrazole forms a large number of alkyl derivatives, the following being some of the general methods for their synthesis:—

(1) *β*-Diketones or *β*-ketonealdehydes of the general formula R·CO·CHR′·COR″ (R, R′, R′ are positive or negative radicles or hydrogen) react with hydrazine or its primary aromatic derivatives, yielding hydrazones which readily undergo further condensation forming pyrazole derivatives, thus:—



This is the best and most general method (Knorr, Annalen, 1887, 238, 137; *see* also D. R. P. 33536; Knorr and Blanks, Ber. 1885, 18, 311, 2256; Claisen and Roosen, *ibid.* 1891, 24, 1888).

(2) Hydrazine also reacts with ketones of the formula R·C : CO·R′, and with aldehydes and ketones of formula R·CO·CR′ : CHR″, to form pyrazoles and pyrazolines (Moureu and Brachin, Compt. rend. 1903, 136, 1262).

Pyrazoles containing an alkyl group attached to nitrogen are obtained by treating silver pyrazole with alkyl iodide or by distilling an alkyl iodide of the pyrazole (Knorr, Ber. 1895, 28, 716).

(3) Pyrazolecarboxylic esters may be formed by the action of diazoacetic ester on acetylenedicarboxylic ester (Buchner, Annalen, 1893, 273, 214).

(4) According to Stoermer, pyrazoles may be obtained almost in theoretical yield by the reduction of the pyrazolones with phosphorus tribromide (Ber. 1907, 40, 484; Annalen, 1907, 352, 322).

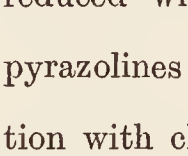
(5) Lactones of the pyrazole series may be prepared by condensing pyrazolones with alkyl acetoacetates (Wolff and Schreiner, Ber. 1908, 41, 550; Bulow and Schaub, *ibid.* 1945).

(6) Pyrazole derivatives may be synthesised by condensing the phenylhydrazone of benzaldehyde or its derivatives with ethyl acetoacetate in presence of zinc chloride (Minunni, Atti R. Accad. Lincei, 1905, [v.] 14, ii. 414; *ibid.* 1906, [v.] 15, i. 19, 136).

(7) Pyrazole compounds containing acid groups attached to nitrogen can be obtained by condensing the sodium derivatives of 5-chloro-3-methyl- and 5-chloro-3-phenylpyrazoles with halogenated fatty esters (Michaelis and Schmidt, Ber. 1910, 43, 2116).

Intensely fluorescent pyrazole derivatives have been prepared by heating 4-hydrazino-1-hydroxyanthraquinone hydrochloride with aniline and aniline hydrochloride, and also by heating dihydrazinoanthraquinone or 1 : 5-disulphohydrazinoanthraquinone with hydrochloric acid (D. R. P. 171293).

The diazopyrazoles readily couple with phenols forming azo dyestuffs. When the pyrazoles obtained from phenylhydrazines are reduced with sodium and alcohol they form pyrazolines



, which on oxidation with chromic or nitric acid, or with ferric chloride in acid solution form red or blue colouring matters (Knorr, Ber. 1893, 26, 100).

The alkyl derivatives of pyrazole are too numerous to be described in detail.

Literature.—Buchner and others, Ber. 1902, 35, 31, 34, 37; Eng. Pat. 22064, 1904; J. Soc. Chem. Ind. 1905, 43; Michaelis and Behn, Ber. 1900, 33, 2595; Michaelis and Hepner, *ibid.* 1903, 36, 3271; Sachs and Alsleben, *ibid.* 1907, 40, 664; Wislicenus and Breit, Annalen, 1907, 356, 32; Michaelis and Klopstock, *ibid.* 354, 102; Auwers, *ibid.* 1911, 378, 210; Michaelis, *ibid.* 293; Michaelis and Lochwitz, Ber. 1910, 43, 2106; Bülow, *ibid.* 1911, 44, 601; Bauer and Dieterle, *ibid.* 2697; Mohr, J. pr. Chem. 1909, [ii.] 79, 1; Mohr, Kraft, Marx, &c. *ibid.* 1914, [ii.] 90, 509; Curtius and Heynemann, *ibid.* 1915, [ii.] 91, 39; Michaelis and Rojahn, Ber. 1917, 50, 737; Dains and Harger, J. Amer. Chem. Soc. 1918, 40, 562.

PYRAZOLIDINES $NH\langle^{CH_2—CH_2}_{NH—CH_2}$, the parent substance is not known, and the derivatives, too, although numerous, have been little investigated owing to their instability. They may be obtained by the action of sodium phenylhydrazine or its derivatives on trimethylene bromide

$$C_6H_5NH\cdot NHNa+CH_2Br\cdot CH_2\cdot CH_2Br = C_6H_5N\langle^{CH_2\cdot CH_2}_{NH\cdot CH_2} + NaBr + HBr$$

(Michaelis and Lampe, Annalen, 1893, 274, 317 ; *see* also Tafel and Pfeffermann, Ber. 1903, 36, 221 ; Buchner and Perkel, *ibid.* 3774 ; Prager, *ibid.* 1452 ; Japp and Michie, Chem. Soc. Trans. 1903, 307). They are energetic reducing agents, and are readily oxidised to pyrazolines.

PYRAZOLIDONE $NH\langle^{CO—CH_2}_{NH—CH_2}$ or $NH\langle^{CH_2\cdot CH_2}_{NH\cdot CO}$ is obtained by agitating hydrazine hydrate with acrylic acid in the cold. It has b.p. 134°, is insoluble in soda and is readily transformed into pyrazolone by oxidation (Rothenburg, J. pr. Chem. 1887, [ii.] 51, 72).

The 3- and the 5- derivatives may be obtained by condensing phenyl or other derivative of hydrazine with acrylic, crotonic, propionic, butyric, or other acids and their derivatives (Rothenburg, Ber. 1893, 26, 2994 ; Knorr and Duden, *ibid.* 108 ; Stolz, *ibid.* 1895, 28, 630 ; Kopisch, *ibid.* 1894, 27, 3111 ; Harries and Loth, *ibid.* 1896, 29, 517 ; Prentice, Chem. Soc. Trans. 1904, 1667 ; Japp and Mayland, *ibid.* 1490 ; *see* also Michaelis and Schenk, Ber. 1907, 40, 3568 ; Bulow and Weedlich, *ibid.* 4326 ; Muckermann, *ibid.* 1909, 42, 3449).

PYRAZOLINE $NH\langle^{N=CH}_{CH_2—CH_2}$, may be obtained by dropping an ethereal solution of acrolein (1 mol.) into an ethereal solution of hydrazine (a little over 1 mol.). The ether is then evaporated, the residue saturated with concentrated hydrochloric acid at 70°, filtered, and evaporated. The salt is dissolved in absolute alcohol, reprecipitated with ether and decomposed with potash (Curtius and Wirsing, J. pr. Chem. 1894, [ii.] 50, 538). When ethylene acts on diazomethane CH_2N_2 pyrazoline is formed (Azzarello). Pyrazoline is a liquid, b.p. 144°, evolves ammonia when boiled with potash, and is oxidised to pyrazole when treated with bromine. It forms a *hydrochloride*, m.p. 130°, a *platinichloride*, and a *picrate*, m.p. 130°.

Its derivatives may be obtained as above (Fischer and Knoevenagel, Annalen, 1887, 239, 197) ; also by the reduction of the corresponding pyrazole, pyrazolidone, or pyrazolidine ; by treating the hydrazones of unsaturated aldehydes and ketones containing a double linking in the α- position, with hot glacial acetic acid (Auwers and Müller, Ber. 1908, 41, 4230 ; Auwers and Voss, *ibid.* 1909, 42, 4411), and by the action of unsaturated ketones on diazomethane (Azzarello, Atti R. Accad. Lincei, 1905, [v.] 14, ii. 229).

For the various derivatives, *see* Klages, J. pr. Chem. 1902, [ii.] 65, 387 ; Balbiano, Gazz. chim. ital. 1888, 81, 371 ; Knorr, Ber. 1893, 26, 102, 108 ; *ibid.* 1895, 28, 712 ; Harries, Annalen, 1901, 319, 233 ; Buchner and Schröder, Ber. 1902, 35, 789 ; Moureu and Lazennec, Compt. rend. 1906, 143, 1239 ; Maire, Bull. Soc. chim. 1908, iv. 3, 272 ; Kijner, J. Russ. Phys. Chem. Soc. 1912, 44, 848 ; Bülow, Ber. 1911, 44, 3710 ; *ibid.* 1912, 45, 528, 3349 ; Buchner, *ibid.* 1912, 45, 117 ; Darapsky, *ibid.* 1912, 45, 797 ; 1913, 46, 218, 863 ; Kishner, J. Russ. Phys. Chem. Soc. 1913, 45, 957 ; Curtius and Boucarl, J. pr. Chem. 1915, [ii.] 91, 39. For phenomena of luminescence in pyrazoline derivatives, *see* Straus, Muffat and Heitz, Ber. 1918, 51, 1457.

The pyrazolines are much more unstable than the pyrazoles, the parent substance pyrazoline being the most stable. They behave as weak bases and have many of the properties of unsaturated aliphatic compounds, of hydrazones and of aldazines.

With oxidising agents many of them yield characteristic red or blue dyestuffs.

PYRAZOLONE $C_3H_4N_2O$ can exist in the two modifications $NH\langle^{CO\cdot CH_2}_{N:CH}$ (5-pyrazolones) and $NH\langle^{CH:CH}_{NH\cdot CO}$ (3-pyrazolones) and many derivatives of each of these have been obtained.

3-**Pyrazolone** is only known in the form of its derivatives, which may be readily obtained by the condensation of acetoacetic ester and acetyl- or benzoyl-phenylhydrazine in the presence of phosphorus trichloride (Mayer, Ber. 1903, 36, 717).

1-**Phenyl-5-methyl-3-pyrazolone**

$$NPh\langle^{NH\ .\ CO}_{CMe:CH}$$

m.p. 166°, b.p. 344°–345°, is best obtained by the action of phosphorus pentachloride on a mixture of acylphenylhydrazine and ethyl acetoacetate (Michaelis, Annalen, 1905, 338, 267). It has both acid and basic properties, and with phosphorus oxychloride, yields 3-chloro-1-phenyl-5-methyl pyrazole, m.p. 295°. It also exists in a labile form, m.p. 157°, and gives a number of acyl and other derivatives.

By condensing ethyl ethoxymethylenemalonate with acetyl phenylhydrazine in the presence of phosphorus tri- or oxy-chloride, a product is produced which, when saponified, yields 1-*phenyl*-3-*pyrazolone carboxylic acid*, m.p. 216°. This on distillation loses carbon dioxide, forming 1-*phenyl*-3-*pyrazolone*, glistening leaflets, m.p. 155°–156° (Michaelis and Remy, Ber. 1907, 40, 1020).

$$OEtCH(CO_2Et)_2+(NH)_2PhCOMe = EtOH+MeCO_2Et+CO_2EtC\langle^{CH\cdot NPh}_{CO\cdot NH}$$

$$\rightarrow CO_2H\cdot C\langle^{CH\cdot NPh}_{CO\cdot NH} \rightarrow CH\langle^{CH\cdot NPh}_{CO\cdot NH}$$

1-**Aryl**-3- or 5-**halogen methyl**-2 : 4-**dialkyl**-3-**pyrazolones** have been obtained by the action of a halogen on the corresponding 5-pyrazolone

when a dihalide is formed, from which on elimination of halogen hydride, the 3-pyrazolone is produced (D. R. P. 208593).

The 3-pyrazolones differ from the 5-isomerides in yielding with sodium nitrite green nitroso derivatives, which, on reduction, yield stable amino derivatives, whereas the 5-pyrazolones yield red-yellow *iso*nitroso derivatives, which on reduction yield unstable amino- pyrazolones. The 3-pyrazolones only react in the hydroxylic form, but the 5-pyrazolones sometimes behave as carbonyl compounds. For many 3-pyrazolone derivatives, *see* Michaelis, Annalen, 1906, 350, 288; *ibid.* 1907, 358, 127; *ibid.* 1910, 373, 129; Kümmel and Remy, Zeitsch. Elektrochem. 1909, 15, 254; Mauthner, Ber. 1908, 41, 2532; Michaelis and Schäfer, Annalen, 1913, 397, 119).

5-Pyrazolone is prepared by heating together hydrazine sulphate (13 parts), sodium formylacetate (20 parts), and caustic soda (200 parts) to 100°. The mixture is acidified with sulphuric acid, rapidly evaporated and extracted with boiling alcohol. The extract is evaporated, redissolved in absolute alcohol and precipitated with ether (Knorr, Ber. 1896, 29, 253). It may also be prepared by the distillation of pyrazolone carboxylic acid (Ruhemann and Morrell, *ibid.* 1895, 28, 988). 5-Pyrazolone forms needle-shaped crystals, m.p. 165°. It sublimes with decomposition, is soluble in water and in alcohol, reduces ammoniacal silver solution, and gives a brown-red colour with ferric chloride.

Pyrazolones may be synthesised by the interaction of hydrazine with acetylenic amides, ammonia being eliminated; thus from phenylpropiolamide $C_6H_5C{:}C{\cdot}CONH_2$ a *phenyl pyrazolone*, m.p. 237°, is obtained; the same product is obtained from the esters of phenylpropiolic or benzoylacetic acids. An *amylphenyl pyrazolone*, m.p. 96°, is obtained by condensing phenyl hydrazine with either ethyl amyl propiolate or caproylacetate. Similarly ethylhexylpropiolate and heptylacetate give an identical *hexylphenylpyrazolone*, m.p. 84°–85°. Pyrazolones are also formed by the interaction of hydrazine or phenyl hydrazine with alkylated β-hydroxyacrylic esters (Moureu and Lazennec, Compt. rend. 1906, 142, 1534).

Pyrazolone derivatives are also formed by the interaction of β-halogen substituted fatty acids or their esters with phenyl hydrazine (Eng. Pat. 9923, 1891; J. Soc. Chem. Ind. 1891, 793; *ibid.* 1893, 463), or by the action of acetyl phenyl hydrazine on malonic acid and its alkyl derivatives in presence of phosphorus trichloride (Michaelis and Schenk, Ber. 1907, 40, 3568; Conrad and Zart, *ibid.* 1906, 39, 2282).

Compounds belonging to the pyrazolone group have been obtained by the action of hydrazine hydrate on dimethylpyrone dicarboxylate (Palazzo and Liverani, Atti R. Accad. Lincei, 1911, [v.] 20, ii. 55).

Of the large number of 5-pyrazolones known, the following may be mentioned:—

1-Phenyl-2-methyl-5-pyrazolone. For derivatives, *see* Michaelis and Kirstein, Ber. 1910, 46, 3603.

1-Phenyl-3-methyl-5-pyrazolone is obtained by the action of phenylhydrazine or its hydrochloride on ethyl acetoacetate (Knorr, Ber. 1883, 16, 2597), and by various other methods (*ibid.* 1894, 27, 1175; D. R. PP. 32277; 77174; Frdl. 1877–87, i. 213; *ibid.* 1894–97, iv. 1198; Bougert, Compt. rend. 1901, 132, 974). It forms prismatic crystals, m.p. 127°, b.p. 287°/205 mm., and unites with both acids and bases. It condenses with ketones, with hydroxy aldehydes (Tambor, Ber. 1900, 33, 864), with diazotised primuline to form azo colouring matters (D. R. P. 117575; *see* also D. R. P. 134162), and is also employed in the manufacture of antipyrin. It forms a large number of derivatives, but unlike antipyrin, it does not combine with phenols or hydroxy acids (Patein, Compt. rend. 1897, 124, 234). For condensations with the nitrobenzaldehydes *see* Heiduschka and Rothacker, J. pr. Chem. 1911 [ii], 84, 533. When boiled with excess of phenyl hydrazine or when the silver salt is treated with iodine, it is converted into bis-phenylmethylpyrazolone

$$NPh\langle\begin{matrix}CO\text{——}\\N:CMe\end{matrix}\rangle CH:CH\langle\begin{matrix}\text{——}CO\\CMe:N\end{matrix}\rangle NPh$$

which when treated with ferric chloride or with sodium nitrite and sulphuric acid, yields *pyrazole blue* $NPh\langle\begin{matrix}CO\text{——}\\N:CMe\end{matrix}\rangle C:C\langle\begin{matrix}\text{——}CO\\CMe:N\end{matrix}\rangle NPh$, violet needles, which resemble indigo in constitution and many properties, but is not so stable, and is of no tinctorial value (Knorr, Annalen, 1887, 238, 171; Knorr and Duden, Ber. 1892, 25, 765). Pyrazole blue is also formed by the direct oxidation of the pyrazolone with ferric chloride (Feist, Annalen, 1906, 345, 100).

4-Bromo-4-nitro-1-*p*-bromophenyl-3-methyl-5-pyrazolone, dark yellow prisms, m.p. *circa* 85° (decomp.) (Wislicenus and Göz, Ber. 1911, 44, 3191). On heating it is converted into 4-keto-1-*p*-bromophenyl-3-methyl-5-pyrazolone

$$C_6H_4Br{\cdot}N\langle\begin{matrix}CO{\cdot}CO\\\|\\N\text{—}CMe\end{matrix}$$

prisms, yellowish-red in transparent, bluish-red in reflected light, m.p. after sintering 171°–172°.

Pyrazolones containing a free hydroxyl group are of technical importance for the preparation of dyes and pharmaceutical products, and can be prepared by the action of acetoacetic ester on the hydrazines of amino-phenols. *1 : 2′-hydroxy-5′-sulphophenyl-3-methyl-5-pyrazolone*

$$SO_3H{\cdot}C_6H_3(OH){\cdot}N\langle\begin{matrix}N:CHMe\\CO{\cdot}CH_2\end{matrix}$$

is obtained by diazotising 2-amino-*p*-phenolsulphonic acid, reducing to 2-hydrazino-*p*-sulphonic acid, which is treated with ethyl acetoacetate in concentrated aqueous solution. Forms colourless crystals. *1 : 3′ : 5′-Dichloro-2′-hydroxyphenyl-3-methyl-5-pyrazolone*

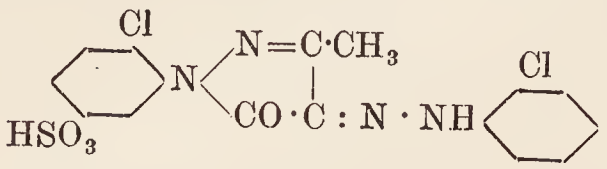
$$OH{\cdot}C_6H_2Cl_2{\cdot}N\langle\begin{matrix}N{=}CMe\\CO{\cdot}CH_2\end{matrix}$$

is prepared in like manner from 4 : 6-dichloro-*o*-aminophenol, whilst 4-chloro-2-amino-*o*-phenol sulphonic acid furnishes 1 : 5′-chloro-2′-hydroxy-3′-sulphophenyl-3-methyl-5-pyrazolone

$$SO_2H{\cdot}C_6H_2Cl(OH){\cdot}N\langle\begin{matrix}N{=}CMe\\CO{\cdot}CH_2\end{matrix}$$

(D. R. P. 249626). For reaction products from 1-phenyl-3-methyl-5-pyrazolone and phthalic anhydride, *v.* Schultz and Rohde (J. pr. Chem. 1913, [ii.] 87, 119). From ethyl oxalate, *v.* Wislicenus, Elvert and Kurtz (Ber. 1913, 46, 3395). With anhydrides, Chatterjee and Das (J. Amer. Chem. Soc. 1919, 41, 707); with aldehydes, Chatterjee and Ghosh (Proc. Asiatic Bengal Soc. 1919, 15, 132).

1-*o*-**Chlorophenyl-3-methyl-5-pyrazolone-***m*-**sulphonic acid** combines with diazo-*o*-chloroaniline, forming the dyestuff



The latter may also be produced by other methods and dyes unmordanted wool fast clear yellow shades (U.S. Pat. 982050, 1911; J. Soc. Chem. Ind. 1911, 412).

1-*p*-**Sulphophenyl-3-methyl-5-pyrazolone** condenses with diazotised *m*-xylidine-*o*-sulphonic acid forming a yellow dye. Similar compounds are given by the tolyl and carboxyl derivatives of the pyrazolone and by 1-phenyl-3-methyl-5-pyrazolone, all of them being distinguished for their beautiful shade and fastness to light (D. R. P. 176954).

4-**Sulphonamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone** is obtained by the action of sodium hydrogen sulphite on 4-nitroso-1-phenyl-2 : 3-dimethyl 5-pyrazolone, the free acid being subsequently precipitated by hydrochloric acid (D. R. P. 193632).

1-*p*-**Dialkylaminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolones** are said to be of therapeutic value, being strong antipyretics. They are produced by alkylating 1-*p*-aminophenyl-2 : 4-dimethyl-3-hydroxymethyl-5-pyrazolone with methyl-iodide or sulphate. A number of these substances and their derivatives and similar compounds are described in D. R. PP. 214716; 217557; 217558; *see* also J. Soc. Chem. Ind. 1909, 854.

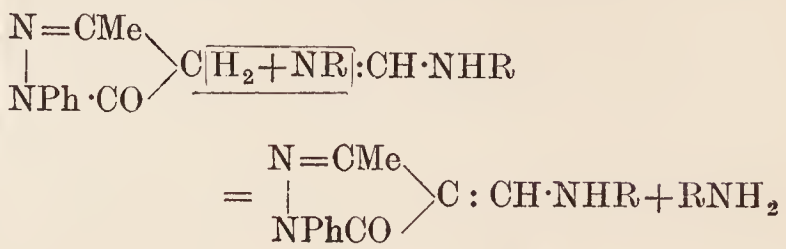
1-*p*-**dimethylaminophenyl-2 : 3 : 4-trimethyl-5-pyrazolone,** which is used in medicine, may be formed by methylating 1-*p*-aminophenyl-3 : 4-dimethyl-5-pyrazolone or other suitable pyrazolone or pyrazole derivative. It is said to be less toxic than the corresponding 2 : 3-dimethyl derivative, but equally active therapeutically (D. R. P. 238256; J. Soc. Chem. Ind. 1911, 1333).

1-**Phenyl-2 : 3-dimethyl-4-isovaleramino-5-pyrazolone** and its bromo derivative are described in D. R. PP. 238373; 227013; J. Soc. Chem. Ind. 1911, 49, 1333.

Greenish-yellow dyestuffs fast to light have been obtained by combining the hydrazine of 3-chloro-2-amino-1-methylbenzene-5-sulphonic acid (1 mol.) with oxalyl acetic ester. The resulting pyrazolone is saponified and treated with another molecule of the diazo derivative of the above sulphonic acid (Eng. Pat. 1244, 1909).

When 1-phenyl- or tolyl-2 : 3-dimethyl-5-pyrazolone and *o*- or *p*-toluene sulphonamide are fused together in molecular proportions, crystalline compounds of therapeutic value are formed (D. R. P. 229814).

Phenylmethyl pyrazolone and the formamidines react smoothly thus



forming red or yellow *aminoethylene pyrazolones*. A number of these are described by Dains and Brown (J. Amer. Chem. Soc. 1909, 31, 1148).

Soap-like compounds have been obtained by combining 1 mol. of dimethyl pyrazolone with 2 mols. of higher fatty acids, and dissolving the product in a neutral fat (D. R. P. 171421; J. Soc. Chem. Ind. 1907, 33).

Literature on 5-pyrazolone derivatives: Kufferath, J. pr. Chem. 1901, [ii.] 64, 334; Walther and Rothacker, *ibid.* 1906, [ii.] 74, 207; Heiduschka and Rothacker, *ibid.* 1909, [ii.] 80, 289; Curtius and Gockel, *ibid.* 1911, [ii.] 83, 279; Mackerman, *ibid.* 513; *ibid.* 84, 278; Betti, Gazz. chim. ital, 1906, 36, ii. 427; *ibid.* i. 178; Knorr, Ber. 1906, 39, 3265; Bülow and Busse, *ibid.* 2459, 3861; Eibner and Laue, *ibid.* 2022; Michaelis and Schlecht, *ibid.* 1954; Emmerling and Kristeller, *ibid.* 2450; Bülow and Schaub, *ibid.* 1908, 41, 2180; Michaelis and Schenk, *ibid.* 3865; Bülow and Haas, *ibid.* 1910, 43, 2647; Michaelis and Lachwitz, *ibid.* 2106; Benary, *ibid.* 1065; Bülow and Göller, *ibid.* 1911, 44, 2835; Michaelis, Annalen, 1911, 385, 1; Ruhemann, Chem. Soc. Trans. 1907, 1363; Castellana, Atti R. Accad. Lincei, 1907, [v.] 16, i. 767; Eng. Pats. 9268, 1897; 22391, 1900; 13383, 27485, 1907; Fr. Pats. 362465, 378486, 1907; 398602, 1909; D. R. PP. 233068; 206637; 180120; 189842; 75378; J. Soc. Chem. Ind. 1895, 987; *ibid.* 1897, 160; *ibid.* 1902, 67; *ibid.* 1906, 714; *ibid.* 1907, 1215; *ibid.* 1908, 91, 420; *ibid.* 1909, 328, 832; *ibid.* 1910, 1099; Wislicenus, Elvert and Kurtz, Ber. 1913, 46, 3395; D. R. PP. 259503–259577; Ruggli and Hartmann, Helv. Chim. Acta, 1920, 3, 493; Wolff and Thielepape, Annalen, 1920, 420, 275; Saunders, Chem. Soc. Trans. 1920, 117, 1264.

Antipyrin (1-phenyl-2 : 3-dimethyl-5-pyrazolone) $C_6H_5N\begin{cases}CO\text{—}CH\\ \|\\ NCH_3\cdot CCH_3\end{cases}$ was discovered by Knorr in 1883, and was introduced into medical use by Filehne. It may be prepared by a variety of methods; thus by heating phenylmethyl pyrazolone with methyl alcohol and methyl iodide (Knorr, Ber. 1884, 17, 549, 2037); by heating 1-phenyl-3-methyl-5-ethoxypyrazole with methyl iodide (D. R. P. 72824; Frdl. 1890–94, iii. 936); by heating the esters of β-halogencrotonic acid with methylphenyl hydrazine (*ibid.* 928; D. R. P. 64444); but is perhaps best manufactured by heating phenylhydrazine with ethyl acetoacetate. The resulting product is dissolved in methyl alcohol and treated with hydrogen iodide. The addition product thus formed is decomposed with sodium hydroxide, and the antipyrin which separates at first as a heavy oil is recrystallised from toluene or ether (J. Soc. Chem. Ind. 1892, 838). It may also be obtained by the direct action of methylphenyl

hydrazine on ethyl acetoacetate. For other methods, *see* D. R. P. 95643; Stolz, J. pr. Chem. [ii.] 55, 148; Michaelis and Pasternack, Ber. 1899, 32, 2406; Frdl. 1894–97, iv 1192; J. Soc. Chem. Ind. 1891, 656.

Antipyrin forms almost inodorous, mildly bitter, lustrous crystals, m.p. 113°, which, when further heated, turn red, then brown, and acquire an odour resembling amber oil. It has b.p. 141°–142° *in vacuô*, 319°/174 mm. (corr.) (Krafft and Weilandt, Ber. 1895, 29, 2241; Knorr, Annalen, 1896, 293, 1). At 25° it dissolves in less than 1 part of water, in 1 of alcohol or chloroform, and in about 30 of ether.

Tests.—Antipyrin gives a deep red colour with ferric chloride, changing to chrome yellow on addition of sulphuric acid (Monferrino, Chem. Zentr. 1909, i. 2029).

Two c.c. of a 1 p.c. solution treated with 2 drops of fuming nitric acid, acquire a green colour which, when boiled and treated with another drop of acid, changes to red, or, if before boiling 5 c.c. of sulphuric acid is added, a cherry-red ring is formed (Sperling, Chem. Zentr. 1906, i. 1118). With nitrous acid it gives a green coloration (Reichard, Chem. Zeit. 1904, 28, 339).

The following reagent gives a very delicate test for antipyrin, 1 grm. vanillin+6 grms. hydrochloric acid diluted with an equal volume of water, +100 grms. 95 p.c. alcohol. Two c.c. of this mixture is poured over a very small crystal of antipyrin and evaporated on the water-bath. A deep orange ring and then a deposit of the same colour is formed; pyramidone does not react thus, and kryogenine gives a yellow-green tint under the same conditions (Primot, Pharm. J. 1909, 83, 9).

For other tests, *see* Jolles, Zeitsch. anal. Chem. 1898, 37, 441; Berenger, Pharm. J. 1904, 72, 117; Steensma, Apoth. Zeit. 1907, 22, 819; Bourcet, Bull. Soc. chim. 1905, [iii.] 33, 572.

Steensma's reagent is prepared by dissolving 1 grm. of *p*-dimethylamino benzaldehyde in 100 c.c. of a solution of 5 c.c. of 25 p.c. hydrochloric acid in 100 c.c. of absolute alcohol. When a liquid containing a trace of antipyrin is evaporated to dryness, together with 5 c.c. of this reagent a rose-red colour is developed (*cf.* Lander and Winter, Analyst, 1913, 97).

Antipyrin may be determined quantitatively thus: A quantity of the sample containing about 0·5 grm. of antipyrin is dissolved in 50 c.c. of water, 5–6 c.c. of N/1 hydrochloric acid is added and the whole heated to boiling. The hot solution is then treated with about 10 c.c. of cold saturated alcoholic picric acid, shaken, and allowed to stand for a few hours, when fine long needles of the picrate separates. The precipitate is collected on a weighed filter, adhering crystals being washed on the filter with the filtrate. They are then drained with a filter pump without washing, and dried at 90°–95° (Riedel, Pharm. J. 1907, 78, 457; *see* also Lemaire, *ibid.* 1905, 74, 13; Schaack, J. Soc. Chem. Ind. 1895, 199, 773; Schuyten, *ibid.* 1073; Kippenberger, Zeitsch. anal. Chem. 1896, 35, 659; *cf.* Emery and Palkin, J. Ind. and Eng. Chem. 1915, 7, 519).

Antipyrin is a valuable analgesic. It has been employed successfully in the various forms of nerve pain, and is said to be remarkably efficient in the treatment of migraine, the lancinating pains of locomotor ataxia, in sciatica, and in various neuralgias resulting from nervous depression or antecedent disease. In fevered states it acts as a fairly constant antipyretic. It is also antiseptic, and it has been used in the treatment of various diseases (Seé, Compt. rend. 1887, 105, 103; Jonescu, Chem. Zentr. 1906, i. 1794; Kobert, *ibid.* 1907, i. 1804; Cervello, Arch. exp. Path. Pharm. 1910, 62, 357; *ibid.* 1911, 64, 403). For its action on the blood, *see* Piccinini, Chem. Zentr. 1911, ii. 1468.

Antipyrin forms compounds with mercury, zinc, iron, and other metallic salts (Schuyten, Chem. Zentr. 1901, ii. 1362; Eury, *ibid.* 1908, ii. 1037; Garelli and Barbieri, Gazz. chim. ital. 1906, 36, ii. 168; Moulin, Bull. Soc. chim. 1903, [iii.] 29, 201; Astre and Vidal, *ibid.* 1905, 33, 842; *ibid.* 1911, iv. 9, 836, 309; Compt. rend. 1900, 130, 837, 1256; J. Soc. Chem. Ind. 1895, 595; Calzolari, Boll. chim. farm. 1911, 50, 763).

Ferripyrin $(C_{11}H_{12}N_2O)_3FeCl_3$, or

$$3C_{11}H_{12}N_2O,2FeCl_3$$

(Calzolari) prepared by mixing an alcoholic solution of ferric chloride with an alcohol ether solution of antipyrin, forms an orange-red powder which is employed in medicine both internally and externally. Ferric bromide gives a similar compound.

Antipyrin oil (*mercuric iodide antipyrin*) is a bright yellow viscous liquid, sp.gr. 1·3518 at 18°, forming an alkaline aqueous solution and readily soluble in alcohol and in acetone. A white precipitate is formed when treated with sulphuric or hydrochloric acid, or with undistilled water and when boiled with distilled water. It is decomposed when heated and when treated with concentrated sulphuric acid, forming red crystals and liberating iodine. When heated with acetic acid it forms a pale yellow compound, m.p. 133° (Raikow and Külümow, Chem. Zentr. 1905, ii. 1595).

Antipyrin also forms arsenates and phosphates (Aubouy, Bull. Soc. chim. 1908, [iv.] 3, 388), and combines with the halogens and halogen acids (Reychler, *ibid.* 27, 612; Michaelis and Pasternack, *l.c.*; Fichter, J. pr. Chem. 1906, [ii.] 74, 297; Schwabe, Ber. 1900, 33, 2609; Knorr, Annalen, 1887, 238, 216). It also forms a cacodylate and methylarsinate (Barthe, Pharm. J. 1915, 94, 99; *ibid.* 1915, 95, 99).

Iodoantipyrin is formed by the action of iodochloride on antipyrin, or of iodine on the latter in presence of sodium acetate, and crystallises in colourless glistening needles, m.p. 160° (Bougault, Chem. Zentr. 1900, i. 507). It combines the properties of iodine and of an antipyretic.

Its formation may be used as a method of estimating antipyrin (*cf.* Analyst. 1914, 39, 480). For a description of the various periodides, *see* Emery and Palkin (J. Amer. Chem. Soc. 1916, 38, 2166). For the behaviour of iodoantipyrin with potassium iodide and hydrochloric acid, *see* Bougault (Ann. Chim. anal. 1919, [ii.] 1, 254).

Nitro- and amino-antipyrins are described by Michaelis (Annalen, 1911, 378, 293).

The most important amino derivative is the

4-dimethyl amido-antipyrin or *pyramidone*, which has a similar physiological action to antipyrin, but has a more powerful and lasting effect on the nervous system than the latter.

Dimethyl- and diethyl-aminoantipyrin is obtained by heating aminoantipyrin hydrochloride with chloro- or bromoacetic or propionic acid and sodium carbonate. The product is then treated with 10 p.c. sulphuric acid and subsequently with caustic soda (Eng. Pat. 26353, 1902; J. Soc. Chem. Ind. 1904, 35).

Pyramidone is also formed by reducing an acetic acid solution of *iso*nitrosoantipyrin, the amino antipyrin formed is then treated with methyl chloride or iodine (Kollo, Pharm. J. 1911, 86, 711); or by methylating acyl or alkyl derivatives of 4-amino-1-phenyl-3-methyl-5-pyrazolone, the acyl or alkyl group attached to a nitrogen or pyrazolone oxygen atom, being readily eliminated (D. R. P. 189842). Pyramidone is an almost tasteless, yellowish-white, crystalline powder, m.p. 108°, soluble in 10 parts of water. It may be distinguished from antipyrin by the fugitive violet blue colour formed when either ferric chloride, nitrous or fuming nitric acid is added (Monferrino, Chem. Zentr. 1909, i. 2029; for other tests, *see* Moulin, Ann. Chim. anal. 1911, 16, 220; J. Soc. Chem. Ind. 1900, 778; Kollo, *l.c.*; also tests for antipyrin). For certain microchemical reactions of pyramidone, *see* J. Soc. Chem. Ind. 1906, 1171).

Pyramidone may be estimated by treating its solution with a measured excess of picric acid, then titrating the excess of the latter with caustic soda (Astruc and Pégurier, Chem. Zentr. 1905, ii. 927, 1554; *see* also Lemaire, Ann. Chim. anal. 1910, 15, 307).

For its microchemical detection, *see* Mayrhofer (Chem. Zentr. 1918, i. 1196).

Acetanilide is sometimes found as an impurity both in antipyrin and in pyramidone, and may readily be detected by the abnormal melting-point of the mixtures (Saporetti, Boll. Chim. Farm. 1909, 48, 367).

Pyramidone may be detected in antipyrin by treating an acid solution with a few drops of potassium ferricyanide and ferric chloride in presence of hydrochloric acid when an intense blue colour is formed.

Pyramidone hydrochloride has m.p. 143°–144°, the *hydrobromide* has m.p. 170°–171° (Astre and Aubouy, Bull. Soc. chim. 1906, [iii.] 35, 856).

Hydriodic acid acts on pyramidone forming the *hydriodide* $C_{13}H_{17}ON_3,HI$, colourless prisms, m.p. above 200° (decomp.). When iodine is added to the latter, the *periodide*

$$C_{13}H_{17}ON_3,HI,I_2$$

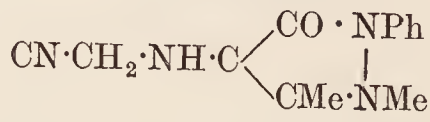
is formed as brown insoluble needles (Cousin, J. Pharm. Chim. 1909, [vi.] 29, 49); other periodides have been formed by Emery and Palkin (J. Amer. Chem. Soc. 1916, 38, 2166).

Pyramidone reacts with Nessler's reagent forming a sulphur yellow crystalline mercuric iodide compound, m.p. 170°–172° (Raikow and Külümow, *l.c.*).

In acid solution it gives a blue coloration with many oxidising substances (nitrites, ferric chloride, hydrogen peroxide, &c.), but if pyridine is added it forms a sensitive reagent for the detection of aneroxydases in blood, raw milk, &c.

The secondary *citrate* of *1-phenyl-2 : 3-dimethyl-4-dimethylamino-5-pyrazolone*, m.p. 85°, is formed by heating 1 mol. of citric acid with 2 mols. of the pyrazolone (D. R. P. 234631; J. Soc. Chem. Ind. 1911, 833).

4-Antipyrylcyanomethylamine

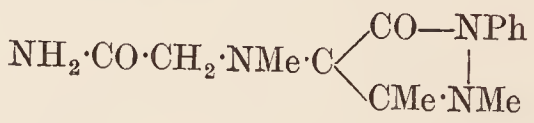


colourless leaflets, m.p. 112°, is formed by treating 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone successively with formaldehyde, sodium hydrogen sulphite and potassium cyanide.

4-Antipyrylaminoacetamide, colourless prisms, m.p. 194°, is obtained by boiling the above methylamine with water or leaving it in contact with concentrated hydrochloric acid. When boiled with the latter it forms a betaine, m.p. above 300°.

4-Antipyrylcyanodimethylamine, colourless crystals, m.p. 75°, is prepared by alkylating the monomethylamine.

4-Antipyrylmethylaminoacetamide



m.p. 158°–159°, is obtained by methylating the above aminoacetamide, whilst *4-antipyrylmethylaminoacetic acid* is similarly prepared from the above betaine. The last three compounds when hydrolysed yield the therapeutically valuable pyramidone (D. R. P. 184850; J. Soc. Chem. Ind. 1907, 947).

Dimethylaminoazoantipyrin, brownish-yellow leaflets, m.p. 107° (rapid heating), 110°–112° (slow heating), may be prepared by coupling dimethylamine with diazoantipyrin. When heated to 130°–140° it yields 1-phenyl-2-methyl-3 : 4-pyrazopyrazol-5-one, orange crystals, m.p. 173°. The corresponding diethyl azoantipyrine forms light brown prisms, m.p. 111°–112° (Stolz, Ber. 1908, 41, 3849).

Antipyrin salicylate (*salipyrin*)

$$C_{11}H_{12}N_2O,C_7H_6O_3$$

formed by fusing together the constituents, is a crystalline powder, m.p. 92°, which is employed as an antiseptic and preservative. Its dimethyl derivative may be formed similarly (Eng. Pats. 10432, 1890; 11040, 1900; J. Soc. Chem. Ind. 1891, 655; *ibid.* 1901, 504; *ibid.* 1902, 272).

Antipyrin mandelate (*Tussol*)

$$C_{11}H_{12}N_2O,C_8H_8O_3$$

formed by mixing solutions of the constituents, is a white crystalline powder, m.p. 53° (Eng. Pat. 11774, 1894; J. Soc. Chem. Ind. 1895, 595).

Antipyrin-β-resorcylate, obtained by the combination of 2 mols. of base and 1 of the acid, forms colourless acid crystals, m.p. 115° (Petit and Févre, Chem. Zeit. 1894, 18, 1094).

Antipyrin valerate, has an unpleasant taste, but is more energetic physiologically than antipyrin (Sochaczewski, J. Soc. Chim. Ind. 1891, 159).

Formopyrin (*Methylene diantipyrin*)

$$(C_{11}H_{12}N_2O)_2CH_2,H_2O$$

prepared by the interaction of antipyrin and formaldehyde, has m.p. 155°–165°, anhydrous, 177°.

Choral antipyrin (*Hypnal*)

$$C_{11}H_{12}N_2O,CCl_3\cdot CH(OH)_2$$

formed by the interaction of the constituents, has m.p. 67°–68°. If the temperature is raised to 100°–110°, it forms the compound

$$C_{11}H_{12}N_2O,CCl_3\cdot CHO$$

m.p. 186°–187°. A dichloral also, m.p. 67°–68°, but more soluble than the mono-, is known (Behal and Choay, Ann. Chim. 1892, [vi.] 27, 330; Patein, Compt. rend. 1897, 125, 956).

Butylchloralantipyrin, formed like hypnal, has m.p. 70° (Calderato, Chem. Zentr. 1902, ii. 1387).

Ethoxyantipyrin $C_{11}H_{11}(OEt)N_2O$ is prepared like antipyrin, ethoxyphenyl hydrazine being used. It has m.p. 91° (Eng. Pats. 2617, 1892; 14716, 1892; J. Soc. Chem. Ind. 1893, 288, 784).

Migraenine is a compound containing 90 parts of antipyrin, 9 of caffeine, and 1 of citric acid (Sleeswijk, Chem. Zentr. 1911, i. 268).

Antipyrin urethane acetamide, m.p. 181°, is described by Lumière and Barbier (Bull. Soc. chim. 1906, [iii.] 35, 123). Antipyrin compounds of piperazine, piperidine, and morpholine have been described by Luft (Ber. 1905, 38, 4044), of camphor sulphonate by Reychler (J. Soc. Chem. Ind. 1902, 987), of saccharin in D. R. P. 131741; Chem. Zentr. 1902, i. 1287. Soluble antipyrin compounds of alkyl glycollic, butyric, and valeric acids are described in D. R. P. 218478. Antipyrin methyl ethyl glycollate, *v.* ASTROLIN; Winzheimer, Pharm. Zeit. 1909, 54, 660.

Antipyrin and xanthydrol unite with elimination of water to form a compound $C_{24}H_{20}O_2N_2$, melting on the maquenne block at 178°–179° (Fabre, J. Pharm. Chim. 1922, 26, 372).

For a number of other compounds of antipyrin, *see* Patein and Dufan, Bull. Soc. chim. [iii.] 15, 172, 609, 849, 1049; Einhorn and Ruppert, Annalen, 1902, 325, 318; D. R. P. 126340.

Tolylpyrin $C_{12}H_{14}N_2O$ is prepared like antipyrin from *p*-tolylhydrazine. It forms colourless, bitter crystals, m.p. 136°–137°, soluble in 14 parts of water at 15° (Knorr, Ber. 1884, 17, 549; Michaelis and Sudendorf, *ibid.* 1900, 33, 2617).

Tolylpyrin salicylate (*Tolysal*), m.p. 100°–101°, is employed in the treatment of nervous derangement and neuralgic pains (Eng. Pat. 19329, 1892; J. Soc. Chem. Ind. 1893, 546). A number of derivatives of tolylpyrin are described by Ebert (Pharm. Zeit. 1893, 38, 251; *see* also Einhorn and Ruppert, *l.c.*; Coblentz, J. Soc. Chem. Ind. 1898, 727).

Homoantipyrin (1-Ph-3-Me-2-ethyl pyrazolone). Sulphides of this and of antipyrin are described by Konek and Norwall (7th Intern. Congr. Appl. Chem. 1909, sect. iv., AI. 234). The corresponding tolyl compound is described in D. R. P. 92009; Frdl. 1894–97, iv. 1198.

*iso***Antipyrin** $MeN\langle \begin{matrix} CO—CH \\ \| \\ NMe\cdot C\cdot C_6H_5 \end{matrix}$, m.p. 108, is formed by heating 3-phenyl-1-methyl-5-pyrazolone (m.p. 207°) with methyl iodide in a sealed tube at 100° (Michaelis, Annalen, 1907, 352, 152, 175). The corresponding *iso*aminoantipyrin, when oxidised with ferric chloride, yields a soluble dyestuff termed *iso**antipyrin red* (the methyl chloride of *iso*rubazonic acid), m.p. 207°

$$CH_3\cdot N\begin{matrix} /C(OH)=\!=\!=C—N=C———CO\backslash \\ \backslash N(CH_3)Cl=CC_6H_5 \quad C(C_6H_5)=N(CH_3)Cl/ \end{matrix} N\cdot CH_3$$

With alkalis it forms a diantipyrylamine. A corresponding antipyrin red is formed by oxidising aminoantipyrin with ferric chloride. It has m.p. 215°, and behaves like the *iso*-compound with alkalis and reducing agents (Michaelis, *ibid.* 213).

*iso***Pyramidone** is best obtained by the action of dimethyl sulphate on amino*iso*antipyrin. It has m.p. 118°, and is less poisonous than ordinary pyramidone (*ibid.* 209). A large number of derivatives of *iso*antipyrin and of *iso*pyramidones are described in the same paper.

3-**Antipyrin** $C_6H_5N\langle \begin{matrix} CMe=CH \\ | \\ NMe—CO \end{matrix}$, m.p. 113°, is formed by treating the corresponding phenyl methyl pyrazolone with methyl alcohol and methyl iodide. It is a powerful antipyretic, and resembles antipyrin very closely, but some of its derivatives have different melting-points (D. R. P. 53834; Lederer, J. pr. Chem. 1892, [ii.] 45, 83; *see* Michaelis, *l.c.*). The corresponding 3-*pyramidone* has m.p. 74°. Derivatives of 3-antipyrin are described by Michaelis (*ibid.* 1907, 358, 127).

Thio-pyrazolones, thio-antipyrins, or **thiopyrins,** in which the oxygen atom is replaced by sulphur have been obtained by the action of potassium hydrogen sulphide on the methochloride or iodide of the required halogen pyrazole (Michaelis and Bindewald, Annalen, 1901, 320, 1; Ber. 1900, 33, 2873); or by the action of phosphorus pentasulphide on the pyrazolones (Stoermer and Johannsen, *ibid.* 1907, 40, 3701).

Like the pyrazolones, thio-pyrazolones condense with benzaldehyde and with ketones in molecular proportions, form coloured azo compounds, and have both acid and basic properties, the former being more strongly pronounced in the thio derivatives. The latter differ from pyrazolones in yielding *ψ*-, not normal alkyl thiopyrins with alkyl iodides, unstable nitroso-compounds, which rapidly change into disulphides, and azo *ψ*-thiopyrins (not normal). On oxidation they do not form bis- compounds, but disulphides or sulphonic acids, and on further oxidation they yield colourless compounds in which two thiopyrazolone groups are united by a sulphur and a carbon linking, and which are, therefore, wholly unlike the constitution of pyrazole blue (Michaelis, Annalen, 1908, 361, 251; *see* also *ibid.* 1907, 352, 187; *ibid.* 354, 55; *ibid.* 358, 127; *ibid.* 1911, 378, 293).

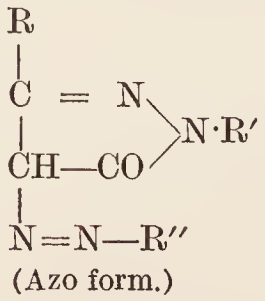
Similar *seleno* derivatives have also been obtained.

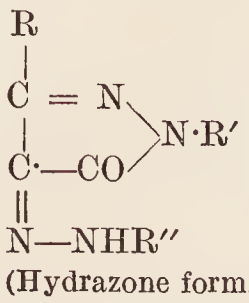
PYRAZOLONE COLOURING MATTERS. Derivatives of pyrazolone, which have substituting groups in the positions 1 and 3, and which are therefore constituted in accordance with the general formula

$$\begin{matrix} & R & \\ (3)\ C & = & N \\ | & & \rangle N\cdot R' \quad (1) \\ (4)\ CH_2 & —CO & / \end{matrix}$$

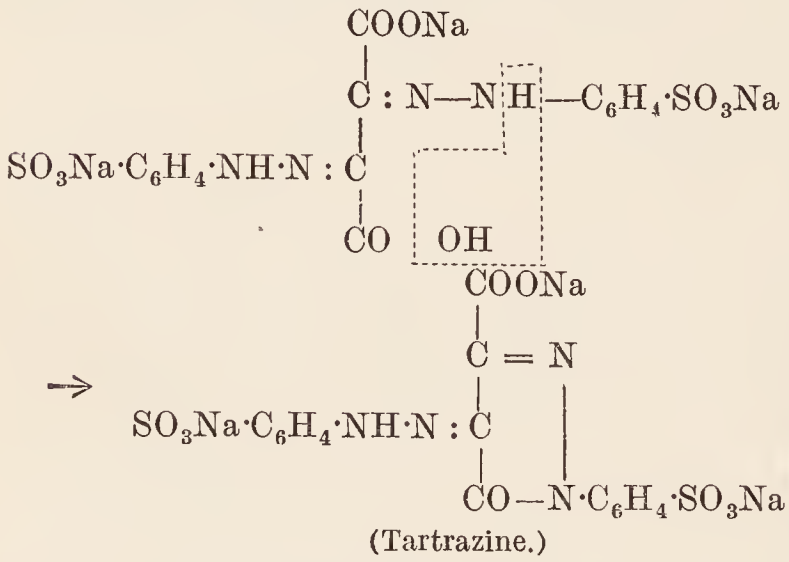
react with diazonium salts yielding azo compounds having the azo residue in the position 4. These compounds are colouring matters and

possess a constitution which is represented by either formula (I.) or (II.)—


(Azo form.)


(Hydrazone form.)

The most important colouring matter of this series is **Tartrazine,** a compound which was prepared by Ziegler (Ber. 1887, 20, 834) by the interaction of phenylhydrazine sulphonic acid and sodium dihydroxytartrate. It is evident that in this reaction, dihydroxytartaric acid behaves as a di-ketone and it was concluded that tartrazine was the corresponding osazone; but Anschutz (Annalen, 1897, 294, 226; 1899, 306, 1; *cf.* also Gnehm and Benda, *ibid.* 1898, 299, 127) has shown that this compound is only an intermediate product in the formation of tartrazine and that the dye is formed from the osazone by the elimination of water thus—


(Tartrazine.)

Tartrazine is therefore the sodium salt of di-*p*-sulphophenylhydrazonopyrazolonecarboxylic acid.

Preparation.—30 kilos. of sodium dihydroxytartrate (*v.* KETONES) are added gradually to a mixture of 33 kilos. of hydrochloric acid and 50 litres of water and dissolved by warming gently, the temperature not being allowed to rise above 30°. The solution is then run into a solution of 50 kilos. of phenylhydrazinesulphonic acid (*v.* HYDRAZINES) in 20 kilos. of sodium carbonate and 70 kilos. of water. The whole is stirred and gradually heated to 80°. After half an hour at this temperature it is allowed to cool, the dye salted out, filtered, and dried.

An alternative process is as follows: To a mixture of 95 kilos. of phenylhydrazinesulphonic acid, 75 kilos. of crystallised sodium acetate, and 500 kilos. of water, 95 kilos. of ethyl oxalate are added at 50°. The whole is heated to boiling for a few minutes and then allowed to cool. To the mass obtained in this way 10 kilos. of caustic soda (40°Bé.) are added, and the mixture is stirred for 3 hours at the ordinary temperature and then at 90°–100° for an hour. The pyrazolone is precipitated by adding a mixture of 8 kilos. of sulphuric acid (96 p.c.) and 32 kilos. of water.

The pyrazolone is now dissolved in 500 kilos. of water and 18·5 kilos. of sodium carbonate, and to the solution is added a paste of diazotised sulphanilic acid prepared by dissolving 9·7 kilos. of sodium sulphanilate in 100 kilos. of water, adding to the solution 3·7 kilos. of sodium nitrite and pouring it into 20 kilos. of hydrochloric acid (20°Bé.) diluted with 100 kilos. of water. After being stirred for 12 hours the mixture is heated, and the colouring matter is salted out, filtered, and dried.

Properties.—Tartrazine, in the form of the trisodium salt, is used as an acid dye for wool. It is a yellow crystalline powder readily soluble in water.

Reactions.—Alcohol precipitates the colour from its aqueous solution; stannous chloride gives a yellow precipitate soluble in oxalic acid. The addition of caustic soda causes the aqueous solution to become darker.

Several other dyes of this class are employed either for dyeing wool or as pigments, and they are prepared by the action of a diazo-compound on a pyrazolone.

Light fast yellow or **Flavazine** is obtained from diazotised aniline and 1-*p*-sulphophenyl-3-methyl-5-pyrazolone, and **Dianil yellow 2R** is similarly prepared from diazotised primulinesulphonic acid (Eng. Pat. 10127 of 1900; U.S. Pat. 656859; Fr. Pat. 300890; D. R. P. 117575).

Flavazine S or **Hydrazine yellow SO** is diazotised aniline combined with 1-*p*-sulphophenyl-5-pyrazolone-3-carboxylic acid (Eng. Pat. 2622 of 1906).

1-Phenyl-3-methyl-5-pyrazolone combined with diazotised toluidine furnishes **Pigment chrome yellow L,** with *o*-toluidine-*m*-sulphonic acid ($CH_3 : NH_2 : SO_3H = 1 : 2 : 5$) **Pigment fast yellow R** (D. R. P. 152862; Fr. Pat. 338531), with *o*-amino-*p*-sulphobenzoic acid **Pigment fast yellow G** (D. R. P. 150125; U.S. Pat. 731670; Fr. Pat. 338531), with primulinesulphonic acid **Dianil yellow R** (Eng. Pat. 10127 of 1900; U.S. Pat. 656857; Fr. Pat. 300890; D. R. P. 117575, and with 1-amino-2-naphthol-4-sulphonic acid **Eriochrome red B** (Eng. Pat. 17274 of 1904; U.S. Pat. 808919; Fr. Pat. 350161; D. R. P. 165743).

The **Xylene yellows** are obtained by combining a diazo-compound (*e.g.* diazotised sulphanilic acid) with 1-*o*-*m*-dichloro-*p*-sulphophenyl-3-methyl-5-pyrazolone (Eng. Pats. 3373 and 12787 of 1908; 113510 of 1917; U.S. Pat. 901675; Fr. Pat. 387245; D. R. P. 222405).

The **Radial yellows** are probably prepared from 3-chloro-*o*-toluidine-5-sulphonic acid [$Cl : NH_2 : CH_3 : SO_3H = 3 : 2 : 1 : 5$] and 1-*p*-sulphophenyl-5-pyrazolone-3-carboxylic acid (Eng. Pat. 1244 of 1909; U.S. Pat. 935370). J. F. T.

PYRENE $C_{16}H_{10}$ occurs with chrysene and other high boiling-point hydrocarbons in the final fraction obtained in the distillation of coal-tar (Graebe, Annalen, 1871, 158, 285); it is also found mixed with fluoranthrene in the so-called 'stupp-fat,' which was obtained as a by-product in the old Idrian process of distilling mercury ores.

Extraction.—(1) From coal tar. The pyrene fraction is treated with carbon disulphide, which dissolves the pyrene and leaves the chrysene and other hydrocarbons. The solution is evaporated and the impure pyrene dissolved in alcohol; on adding an alcoholic solution of picric acid a characteristic insoluble picrate separates out. When this is treated with ammonia, pyrene is

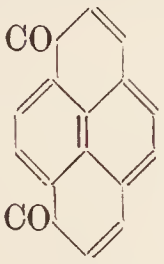
liberated and may be obtained pure by recrystallisation from alcohol.

(2) From stupp-fat. The more soluble impurities are first removed with cold alcohol; the residue is dissolved in boiling alcohol, and the insoluble picrate is prepared as above.

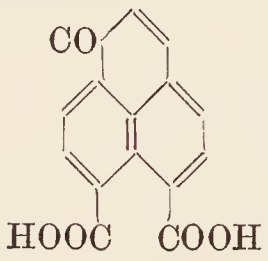
Properties and reactions.—Pyrene forms monoclinic tables melting at 149°; it boils at a temperature higher than 360°. It is moderately soluble in alcohol, considerably more so in toluene, ether, and carbon disulphide. On oxidation with chromic anhydride, pyrenequinone and then pyrenic acid are formed; on reduction hexahydro-pyrene is obtained; on chlorination, mono-, di-, tri-, and tetra- chloro derivatives; on nitration mono-, di-, and tetranitro derivatives; on sulphonation a disulphonic acid are obtained. On treatment with benzoylchloride or with α-naphthoylchloride, in presence of aluminium chloride, *dibenzoylpyrene*, m.p. 155°, *tribenzoylpyrene*, m.p. 235°–237°, or tri-*α*-*naphthoylpyrene*, m.p. 218°–219° are obtained. The di-*α*-tri-*benzoylpyrenes* are separated by fractional crystallisation (Scholl, D. R. P. 239761). *V.* Ferrario and Fels (Chem. Zeit. 1913, 37, 89) for diphenyldiphenylene-pyrene and other derivatives.

Constitution.—Bamberger and Philip (Annalen, 1890, 240, 158) regarded pyrene as containing the naphthalene nucleus to which two benzene nuclei were joined in the peri positions. According to Goldschmidt (Chem. Zentr. 1907, [i.] 1421), and Langstein (*ibid.* 1910, [ii.] 1760), the arrangement of the linkings in the molecule is different, pyrene (I.), pyrene quinone (II.), and pyrenic acid (III.) having the constitutions given below—


I.



II.



III.

Pyrene is also closely related to *thebenol*,

$$OH\cdot C_{14}H_6(OMe)\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}CH_2\\ O\end{matrix}\begin{matrix}>\\ \\ \end{matrix}CH_2$$

from which it is obtained by reduction with zinc dust (Freund, Ber. 1897, 30, 1357, 1374). For the synthesis of pyrene by the condensation of diphenyl-2 : 2-diacetic acid to dihydroxypyrene and reduction of the hydroxy compound, *v.* Weitzenböck (Monatsh. 1913, 34, 193); and for its synthesis from the dianhydride of naphthalene - 1 : 4 : 5 : 8 - tetracarboxylic acid (which reacts with ethyl malonate and zinc chloride at 170° to form a substance which yields pyrene on distillation with zinc dust), *v.* Freund and Fleischer (Annalen, 1913, 402, 77).

PYRENE KETONE *v.* KETONES.

PYRENOL, PYROSAL *v.* SYNTHETIC DRUGS.

PYRETHRIC ACID *v.* RESINS.

PYRETHRIN *v. Pellitory resin*, art. RESINS.

PYRETHRUM ROOT. The dried root of *Anacyclus Pyrethrum* (DC.) *v. Pellitory resin*, art. RESINS.

PYRETOL or **PYRETHRON.** The active principle of 'insect powder' (Pyrethrum flowers). An odourless, non-volatile light yellow resinoid substance extremely toxic to cold-blooded animals. It was first isolated by Sato. It is not, however, a chemical entity, but a mixture which on hydrolysis yields two alcohols, $C_{21}H_{34}O$ and $C_{27}H_{46}O$, a liquid fatty acid, palmitic acid, and another solid fatty acid. Saponification value 216; iodine value 116. Occurs mainly in the ovary at the time of blooming (Yamamoto, J. Tokyo Chem. Soc. 1919). The production of dried pyrethrum flowers and the manufacture of insect powder is almost entirely a Japanese industry, and amounted to about 2000 tons in 1918. It has since fallen off owing to many farmers turning their attention to other crops. The results of analyses of Dalmatian pyrethrum powder, prepared from various species of *Chrysanthemum* flowers, gave the following percentage numbers: moisture, 10·7–10·2; ether extract, 5·1–5·8; ash, 7·4–7·72; crude fibre, 24·56–25·88 (Costa, Giorn. Chim. Ind. Appl. 1922, 4, 91).

PYREX GLASS. A borosilicate glass containing no metals of the magnesia-lime zinc group and no heavy metals. Its softening point is about 800°, or under pressure 600°. Does not devitrify in its working range and has considerable resistance to attack by acids. Possesses excellent properties for electric insulation, good dielectric properties and a tensile strength superior to that of porcelain and is an excellent material for the construction of chemical plant.

PYRIDINE DERIVATIVES, DYESTUFFS, and HOMOLOGUES *v.* BONE OIL. The following physical constants have been published by Heap, Jones and Speckman (J. Amer. Chem. Soc. 1921, 43, 1936): Pyridine b.p. 115·3°; d_4^{25} 0·9776; 2-methylpyridine b.p. 128°–129°; d_4^{25} 0·9404; 3-methylpyridine b.p. 143·8°; d_4^{25} 0·9515; 2 : 6-dimethylpyridine b.p. 137·5°; d_4^{25} 0·9200; 2 : 4-dimethylpyridine b.p. 157·1°; d_4^{25} 0·9273. M. A. W.

PYRIMIDINES or **METADIAZINES** are compounds containing the heterocyclic ring



The earliest known members of the series were termed *cyanalkines*, because they were obtained by the polymerisation of alkyl nitriles by the action of sodium or sodium ethoxide. *Cyanethine* was discovered by Kolbe and Frankland (Annalen, 1848, 68, 269). E. v. Meyer (Ber. 1871, 4, 176; J. pr. Chem. 1883, [ii.] 27, 152; 1889, [ii.] 39, 156; [ii.] 40, 303) prepared the lower homologue *cyanmethine*, and showed that it was a metadiazine, *amino-dimethylmetadiazine* $MeC\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}N:CMe-\\ N\cdot C(NH_2)=\end{matrix}\begin{matrix}>\\ \\ \end{matrix}CH$, and that the hydroxy derivative obtained by the action of nitrous acid (Wollner, *ibid.* 1884, [ii.] 29, 131), *hydroxydimethylmetadiazine*, is identical with the *dimethylhydroxypyrimidine* obtained by Pinner (Ber. 1884, 17, 2519; 1885, 18, 759, 2848; 1887, 20, 2361; 1889, 22, 1612) by the condensation of ethyl acetoacetate and acetamidine

$$NH:CMe\cdot NH_2+CO_2Et\cdot CH_2\cdot COMe$$
$$=NH:CMe\cdot NH\cdot CO\cdot CH_2\cdot COMe+EtOH$$

$NH:CMe\cdot NH\cdot CO\cdot CH_2\cdot COMe$

$$\rightarrow NH\langle\begin{matrix}CO\cdot CH_2\\CMe:N\end{matrix}\rangle CMe\cdot OH$$

$$\rightarrow NH\langle\begin{matrix}CO\cdot CH\\CMe:N\end{matrix}\rangle CMe+H_2O$$

$$NH\langle\begin{matrix}CO\cdot CH\\CMe:N\end{matrix}\rangle CMe \rightarrow N\langle\begin{matrix}C(OH)\cdot CH\\CMe{=}{=}N\end{matrix}\rangle CMe$$

Pinner gave the name *pyrimidine* to the then hypothetical first member of the series, because it stands in the same relation to pyridine as does pyridine to benzene :—

$$CH\langle\begin{matrix}CH\cdot CH\\CH:CH\end{matrix}\rangle CH \qquad CH\langle\begin{matrix}N-\!-CH\\CH:CH\end{matrix}\rangle CH$$

Benzene. Pyridine.

$$CH\langle\begin{matrix}N\cdot CH\\N:CH\end{matrix}\rangle CH$$

Pyrimidine.

Pyrimidine $C_4H_4N_2$ was obtained by Gabriel and Colman (Ber. 1899, 32, 1525) from methyluracil (4-*methyl*-2 : 6-*dioxytetrahydropyrimidine*) by the following series of reactions: methyluracil is converted by the action of phosphoryl chloride into 4-*methyl*-2 : 6-*dichloropyrimidine* $ClC\langle\begin{matrix}N\cdot CMe\\N:CCl\end{matrix}\rangle CH$, this is reduced by zinc-dust and water to 4-*methylpyrimidine*

$$CH\langle\begin{matrix}N\cdot CMe\\N:CH\end{matrix}\rangle CH$$

which, on oxidation with potassium permanganate, yields *pyrimidine*-4-*carboxylic acid*

$$CH\langle\begin{matrix}N\cdot C(CO_2H)\\N{=}{=}CH\end{matrix}\rangle CH$$

from which *pyrimidine* $CH\langle\begin{matrix}N\cdot CH\\N:CH\end{matrix}\rangle CH$ is obtained by distillation. Pyrimidine is more conveniently obtained by reducing with zinc-dust the 2 : 4 : 6-*trichloropyrimidine*

$$ClC\langle\begin{matrix}N\cdot CCl\\N:CCl\end{matrix}\rangle CH$$

obtained by the action of phosphoryl chloride on barbituric acid (2 : 4 : 6-*trioxyhexahydropyrimidine*) (Gabriel, Ber. 1900, 33, 3666; Gabriel and Colman, *ibid.* 1904, 37, 3657); or by similarly reducing 2 : 4 : 5 : 6-tetrachloropyrimidine obtained from alloxan (2 : 4 : 5 : 6-*tetraoxyhexahydropyrimidine*) (Ciamician and Magnaghi, *ibid.* 1885, 18, 3444), or from dialuric acid (2 : 4 : 6 - *trioxy* - 5 - *hydroxyhexahydropyrimidine*) (Emery, *ibid.* 1901, 34, 4178). Pyrimidine is a crystalline compound with a penetrating, stupefying odour, it has m.p. 20°–22°, b.p. 123·5°–124°/762 mm.; it is soluble in water, forming a solution neutral to litmus; the *mercurichloride* and *aurichloride* are crystalline, the latter melts at 226°; the *picrate* forms pale yellow needles, and has m.p. 156°. 2 : 4 : 6-*Trichloropyrimidine* has m.p. 21°, and b.p. 213°/755 mm. (Gabriel, Ber. 1900, 33, 3666); 2 : 4 : 5 : 6-*tetrachloropyrimidine* has m.p. 70°, yields *trichloroiodopyrimidine*, m.p. 93°–94°, and *dichlorodiiodopyrimidine*, m.p. 159°, by the action of sodium iodide; 2 : 4 : 5 : 6-*tetrabromopyrimidine* has m.p. 165°–166° (Emery, *l.c.*). For the preparation of pyrimidines by the use of nitromalonaldehyde *v.* Hale and Brill (J. Amer. Chem. Soc. 1912, 34, 82).

2 : 4 : 6-*Triaminopyrimidine*, m.p. 245°–246°, obtained by the action of alcoholic ammonia on the trichloro compound above 200°, forms crystalline salts, and is converted by fuming nitric and sulphuric acid into 5-*nitro*-2 : 4 : 6-*triaminopyrimidine*, which on reduction yields 2 : 4 : 5 : 6-*tetraaminopyrimidine*, orange-yellow prisms, with no definite melting-point, forming a strongly alkaline solution in water and yielding crystalline salts (Gabriel, Ber. 1901, 34, 3362; 1905, 38, 149; Traube, Ber. 1904, 37, 4544); for the action of alcoholic ammonia at the ordinary temperature on 2 : 4 : 6-trichloropyrimidine, *see* Büttner (Ber. 1903, 36, 2227); 2 : 4-*dichloro*-5-*nitropyrimidine*, obtained by heating 5-nitrouracil with phosphoryl chloride, has m.p. 29·3°, and b.p. 153°–155°/58 mm.; it yields with ammonia 2-*chloro*-5-*nitro*-4-*aminopyrimidine*, m.p. 217°, which can be reduced to 4 : 5-*diaminopyrimidine*. m.p. 202·5°, b.p. 229°/32 mm. (Isay, *ibid.* 1906, 39, 250).

A very large number of pyrimidine derivatives have been prepared, and the chemistry of the group covers a wide field, much of it lying beyond the scope of this present article. Certain of the pyrimidines, *cytosine*, *thymine*, and *uracil*, occur among the degradation products of the proteins; others, including the alkyl derivatives of barbituric acid, have important therapeutic properties; and these merit description.

Cytosine, 2 - *oxy* - 6 - *aminodihydropyrimidine* $C_4H_5N_3O,H_2O$; $CO\langle\begin{matrix}N:C(NH_2)\\NH-\!-CH\end{matrix}\rangle CH$, was discovered by Kossel and Neumann (Ber. 1894, 27, 2215) among the products of hydrolysis of nucleic acid from the thyroid gland, and has been similarly obtained from the nucleic acids of the testicle of the sturgeon and herring (Kossel and Steudel, Zeitsch. physiol. Chem. 1902, 37, 177), and other nucleic acids of both animal and vegetable origin (Inouye, *ibid.* 1905, 46, 201; Mandel and Levene, *ibid.* 1905, 46, 155; 1906, 47, 140; 49, 262; 50, 1; Kossel and Steudel, *ibid.* 1903, 38, 49; Osborne and Heyl, Amer. J. Physiol. 1908, 21, 157; Wheeler and Johnson, Amer. Chem. J. 1903, 29, 505; Schreiner and Lathrop, J. Amer. Chem. Soc. 1912, 34, 1242).

The question has been raised by Burian (Zeitsch. physiol. Chem. 1907, 51, 438), and by Osborne and Heyl (Amer. J. Physiol. 1908, 21, 157), whether the pyrimidine bases from nucleic acid are primary products of hydrolysis or arise from the purine bases by a process of hydrolysis and reduction. The results obtained by Levene and Jacobs, and La Forge (Ber. 1910, 43, 3150; 1911, 44, 1027; 1912, 45, 608), serve to show that these bases are primary products of hydrolysis, for the authors have isolated the pyrimidine nucleotides, *cytidine nucleotide* $PO(OH)_2\cdot O\cdot C_9H_{12}O_4N_3$ and *uridine nucleotide* $PO(OH)_2\cdot O\cdot C_9H_{11}O_5N_2$, by the partial hydrolysis of yeast nucleic acid, and shown that cytidine is a complex containing one molecule of cytosine and one of ribose. *Cytidine* crystallises in long needles, m.p. 230° (decomposition), it has $[\alpha]_D^{21}+29{\cdot}63°$, and forms a sparingly soluble *nitrate*; the *picrate* has m.p. 185°–187°, the *sulphate* m.p. 233°, and the *hydrochloride* m.p. 218°, and the *tribenzoyl* derivative has m.p. 205°. For the brucine salt of cytosine-uracil-dinucleotide, m.p. 200° (corr.), *v.* Levene (J. Biol.

Chem. 1917, 31, 591); *cf.* Jones and Read (*ibid.* 39), who gives m.p. 175°.

Cytosine has been prepared synthetically by Wheeler and Johnson (Amer. Chem. J. 1903, 29, 492, 505) by the following series of reactions: *ψ*-ethylthiocarbamide hydriodide and ethyl sodioformylacetate condense to form 2-*ethylthiol*-6-*oxydihydropyrimidine* $EtS\cdot C\lessgtr^{NH\cdot CO}_{N\cdot CH}\gtrdot CH$, converted by the action of phosphorus pentachloride into 2-*ethylthiol*-6-*chloropyrimidine* $EtS\cdot C\lessgtr^{N:CCl}_{N\cdot CH}\gtrdot CH$, this reacts with alcoholic ammonia to form the 6-*amino* derivative, which yields, on prolonged boiling with hydrobromic acid, 2-*oxy*-6-*aminodihydropyrimidine*

$$CO\lessgtr^{N:C(NH_2)}_{NH\text{---}CH}\gtrdot CH$$

identical with the natural cytosine.

Cytosine crystallises with one molecule of water in thin colourless pearly plates, becomes anhydrous at 100°, blackens at 300°, and decomposes at 320°–325°; it is insoluble in ether, sparingly soluble in alcohol or water, 1 part dissolving in 129 parts of water at 25°.

Cytosine is readily converted into uracil (2 : 6-dioxytetrahydropyrimidine) by the action of nitrous acid, or partially by heating with 20 p.c. sulphuric acid at 150°–170°. Both cytosine and uracil give a characteristic purple colour when dissolved in bromine water, and the solution treated with barium hydroxide solution; the dibromohydroxyhydrouracil first formed is converted by the barium hydroxide into *iso*-dialuric acid, which immediately undergoes a rearrangement in the alkaline solution to give the purple barium salt of dialuric acid (Wheeler and Johnson, J. Biol. Chem. 1907, 3, 183). Cytosine, thymine or uracil gives with diazobenzenesulphonic acid a red solution in the presence of alkali, the colour given by thymine being the most intense (Johnson and Clapp, J. Biol. Chem. 1908, 5, 163).

Salts.—Cytosine forms crystalline salts with acids, and compounds with certain metallic salts (Kossel and Steudel, Zeitsch. physiol. Chem. 1903, 38, 49; Kutscher, *ibid.* 170; Wheeler and Jamieson, J. Biol. Chem. 1908, 4, 111; Wheeler and Johnson, Amer. Chem. J. 1904, 31, 591, 605; Meyers, J. Biol. Chem. 1910, 7, 249); the *hydrochloride* $C_4H_5N_3O,HCl,H_2O$, forms large plates that become anhydrous at 50°, and melt at 275°–279°; the *acid salt*

$$C_4H_5N_3O,2HCl$$

forms flat prisms; the *hydrobromide*

$$C_4H_5N_3O,HBr$$

shining prisms; *nitrate* $C_4H_5N_3O,HNO_3$; *basic sulphate* $(C_4H_5N_3O)_4H_2SO_4,2H_2O$, sparingly soluble needles, decomposes at 323°; *normal sulphate* $(C_4H_5N_3O)_2H_2SO_4,2H_2O$, prisms, m.p. 287°; *acid sulphate* $C_4H_5N_3O,H_2SO_4$, rhombic crystals, m.p. 197°; *phosphate* $C_4H_5N_3O,H_3PO_4$, prisms, m.p. 236°; the *silver nitrate compound* $C_4H_5N_3O,AgNO_3$ forms needles; *platinichloride* $(C_4H_5N_3O,HCl)_2PtCl_4$, sparingly soluble yellow crystals; *picrate* $C_4H_5N_3O,C_6H_3N_3O_7$, yellow shining needles, m.p. 270° (Kossel and Steudel), 300°–305° (Wheeler and Johnson); the *picrolonate* $C_4H_5N_3O,C_{10}H_8N_4O_5$ forms fine needles or prisms, m.p. 270°–273°.

Substituted derivatives.—4-*Chlorocytosine*

$$CO\lessgtr^{N:C(NH_2)}_{NH\text{---}CCl}\gtrdot CH$$

forms small needles, does not melt at 300° (Wheeler and Jamieson, Amer. Chem. J. 1904, 32, 342); 5-*bromocytosine* $C_4H_4ON_3Br$ decomposes at 235° (Wheeler and Johnson, *ibid.* 1904, 31, 591); 5-*iodocytosine* $C_4H_4ON_3I$ decomposes between 225° and 245° (Johnson and Johns, J. Biol. Chem. 1906, 1, 305), its *picrate* $C_4H_4ON_3I,C_6H_3O_7N_3$ decomposes at 247°–257°; 5-*nitrocytosine* $C_4H_4N_3O(NO_2)$, formed by direct nitration of cytosine, crystallises in colourless needles, decomposes at 300°, its *hydrochloride* $C_4H_4O_3N_4,HCl$ does not decompose below 300°; on reduction the nitro derivative yields 5-*aminocytosine* (5 : 6-diamino-6-oxydihydropyrimidine) $C_4H_4ON_3(NH_2),H_2O$, this loses H_2O at 120°–130°, and decomposes above 230° (Johnson, Johns and Heyl, Amer. Chem. J. 1906, 36, 160). 2-*Oxy*-6-*acetaminodihydropyrimidine*, obtained by heating cytosine with acetic anhydride, does not melt at 300° (Wheeler and Johnson, Amer. Chem. J. 1903, 29, 492).

For the synthesis of *cytosine*-4-*aldehyde*, *see* Johnson and Mikeska, J. Amer. Chem. Soc. 1919, 41, 810.

Cytosine-5-*carboxylic acid*

$$CO\lessgtr^{N:C(NH_2)}_{NH\text{---}CH}\gtrdot C(CO_2H)$$

decomposes at 256°–257°, the *amide* does not melt at 310°, the *hydrochloride*, *nitrate*, *sulphate*, and *picrate* are crystalline (Wheeler and Johns, Amer. Chem. J. 1907, 38, 594; 1908, 40, 233).

Cytosine-5-*acetic acid*

$$CO\lessgtr^{N:C(NH_2)}_{NH\text{---}CH}\gtrdot C\cdot CH_2\cdot CO_2H$$

blackens at 240°–250°, does not melt below 290°, the *picrate* has m.p. 217°–218° (Johnson, Peck and Ambler, J. Amer. Chem. Soc. 1911, 33, 758). 4-Phenylcytosine exists in two distinct forms (Johnson and Hemingway, J. Amer. Chem. Soc. 1915, 37, 378).

iso-*Cytosine*, 2-*amino*-6-*oxydihydropyrimidine* $H_2N\cdot C\lessgtr^{NH\cdot CO}_{N\text{---}CH}\gtrdot CH$, prepared by the condensation of ethyl sodioformylacetate with guanidine, crystallises from water in thick prisms, melts at 276° with decomposition (Wheeler and Johnson, Amer. Chem. J. 1903, 29, 492); for the *salts* and *derivatives*, *see* Wheeler and Johnson, Amer. Chem. J. 1903, 29, 492; 1904, 31, 591; Wheeler and Jamieson, J. Biol. Chem. 1908, 4, 111.

4-Phenyl*iso*cytosine exists in four isomeric forms (Johnson and Hall, J. Amer. Chem. Soc. 1914 36, 1201).

Uracil, 2 : 6-*dioxytetrahydropyrimidine*

$$CO\lessgtr^{NH\cdot CO}_{NH\cdot CH}\gtrdot CH$$

was first obtained, together with thymine and cytosine, by the hydrolysis of yeast nucleic acid (Ascoli, Zeitsch. physiol. Chem. 1900, 31, 161), and is similarly formed from other nucleic acids (Kossel and Steudel, *ibid.* 1902, 37, 245; Levene, *ibid.* 1903, 39, 4; Levene and Stookey, *ibid.* 1904, 41, 404); it is also obtained on autolysis of pancreas (Levene, *ibid.* 1903, 37,

527; Reh, Beitr. chem. Physiol. Path. 1903, 3, 569; Jones, Zeitsch. physiol. Chem. 1904, 42, 35; Levene and Mandel, *ibid.* 1906, 49, 262); and forms one of the bases not precipitated by ammoniacal silver nitrate from secale extract (Engeland and Kutscher, Centralbl. Physiol. 1910, 24, 589).

By the partial hydrolysis of yeast nucleic acid, Levene, Jacobs and La Forge (Ber. 1910, 43, 3150; 1911, 44, 1027; 1912, 45, 608) have obtained the *uridine nucleotide*

$$P(OH)_2 \cdot O \cdot C_9H_{11}O_5N_2$$

from which the nucleoside *uridine* $C_9H_{12}O_6N_2$ can be prepared by hydrolysis with ammonia; it can also be obtained by the action of nitrous acid on cytidine. *Uridine* is a complex containing uracil and ribose in molecular proportion, it crystallises in long prismatic needles, m.p. 165°, and has $[\alpha]_D^{30}+5{\cdot}15°$, $[\alpha]_D^{20}+6{\cdot}40°$; 5-*bromouridine* has m.p. 181°–184°, $[\alpha]_D^{21}-15{\cdot}4°$; *hydroxyuridine* has m.p. 222°–223°, the *phenylhydrazide* has m.p. 209°; *dihydrouridine* is a colourless syrup, $[\alpha]_D+39{\cdot}1°$; *cf.* Johnson (J. Amer. Chem. Soc. 1914, 36, 1891).

Uracil-cytosine-dinucleotide $C_{18}H_{25}O_{16}N_5P_2$ is obtained as a white granular powder, $[\alpha]_D+15°$, on heating yeast-nucleic acid with dilute sulphuric acid; the brucine salt

$$C_{18}H_{25}O_{16}N_5P_2,4(C_{23}H_{26}O_4N_2)_{14}H_2O$$

crystallises in needles which sinter at 170° and melt at 175°, Jones and Read (J. Biol. Chem. 1917, 31, 39); *cf.* Levene (*ibid.* 591), who gives m.p. 200°.

Synthesis.—Fischer and Roeder (Ber. 1901, 34, 3751) synthesised uracil from acrylic acid and carbamide, these condense at 210°–220° to form dihydrourucil, which is converted by bromine into bromodihydrouracil, and this loses HBr on heating with pyridine, and yields uracil

$$CH\begin{matrix}<\\<\end{matrix}\begin{matrix}COOH\\CH_2\end{matrix} + \begin{matrix}H_2N\\H_2N\end{matrix}>CO = CO\begin{matrix}<\\<\end{matrix}\begin{matrix}NH\cdot CO\\NH\cdot CH_2\end{matrix}>CH_2 + H_2O$$

$$CO\begin{matrix}<\\<\end{matrix}\begin{matrix}NH\cdot CO\\NH\cdot CH_2\end{matrix}>CHBr \rightarrow CO\begin{matrix}<\\<\end{matrix}\begin{matrix}NH\cdot CO\\NH\cdot CH\end{matrix}=CH$$

Uracil has also been prepared synthetically by Gabriel and Colman (Ber. 1903, 36, 3379) from trichloropyrimidine; and by Wheeler, Merriam, and others (Amer. Chem. J. 1903, 29, 478; J. Biol. Chem. 1905, 2, 105; Amer. Chem. J. 1907, 37, 392; 40, 547) from thiourea and ethyl sodioformylacetate. Uracil forms a colourless crystalline powder consisting of rosettes of fine needles, blackens at 280°, and melts with decomposition at 338°; it is sparingly soluble in cold, and readily soluble in hot water, dissolves readily in ammonia, is insoluble in alcohol or ether, and is not decomposed on boiling with alkalis.

Uracil, like cytosine, gives a characteristic purple colour when dissolved in bromine water, and the solution treated with barium hydroxide solution; and, like cytosine and thymine, gives a red colour with diazobenzenesulphonic acid in the presence of alkali (*v.* CYTOSINE).

Salts.—Uracil forms salts in which one or two atoms of hydrogen are replaced by metals, the *sodium* salt $C_4H_3O_2N_2Na,\frac{1}{2}H_2O$ forms needles from alcohol and water; the *potassium* salt $C_4H_3O_2N_2K,H_2O$, long needles, sparingly soluble in dilute alcohol; the *mercury* $C_4H_2O_2N_2Hg$ and *lead* $C_4H_2O_2N_2Pb$ salts are white precipitates, very sparingly soluble in water (Myers, J. Biol. Chem. 1910, 7, 249; Johnson and Clapp, *ibid.* 1908, 5, 49).

Substituted derivatives.—5-*Chlorouracil*, prepared by the action of chlorine water on uracil, has m.p. 300°–305° (Johnson, Amer. Chem. J. 1908, 40, 19); 5-*bromouracil* has m.p. 293° with decomposition (Wheeler and Merriam, *ibid.* 1903, 29, 478); 5-*iodouracil* has m.p. 272° with decomposition (Johnson and Johns, J. Biol. Chem. 1906, 1, 305); 5-*cyanouracil* forms prisms, m.p. 295° (Johnson, Amer. Chem. J. 1909, 42, 505). 5-*Nitrouracil* forms golden-yellow needles, that decompose without melting; the *potassium*, *ammonium*, *calcium*, *barium*, *zinc*, and *copper* salts are crystalline (Behrend, Annalen, 1887, 240, 1; Behrend and Grünwald, *ibid.* 1899, 309, 254; Johnson, Amer. Chem. J. 1908, 40, 19; Johnson and Matsuo, J. Amer. Chem. Soc. 1919, 41, 782). 5-*Aminouracil* crystallises from water in thick felted needles that decompose without melting; the *nitrate* crystallises with $1H_2O$; the *picrate* has m.p. 247°–248°; the *acetyl* derivative sublimes without decomposition; the *benzoyl* derivative has m.p. 283°–287° (Behrend and Grünwald, *l.c.*; Wheeler and Bristol, Amer. Chem. J. 1905, 33, 437); 4 : 5-*diaminouracil* $C_4H_6O_2N_4$ (Traube, Ber. 1900, 33, 1371); 4 : 5-*diacetyldiaminouracil* sinters at 300° and decomposes at a higher temperature (Boehringer and Söhne, D. R. P. 126797). 2 : 5-*diaminouracil* is identical with *divicine*, which can be obtained from vicine, a nucleoside composed of this pyrimidine with dextrose

$$C_6H_{11}O_6 \cdot N\begin{matrix}<\\<\end{matrix}\begin{matrix}C(NH_2)=N\\CO\cdot CH(NH_2)\end{matrix}>CO$$

(Sevene, J. Biol. Chem. 1914, 18, 305; Sevene and Senior, *ibid.* 1916, 25, 607). Uracil may be quantitatively converted into *hydrouracil*, m.p. 227°, by gaseous hydrogen in presence of colloidal platinum at a pressure of two atmospheres and at 75°–85° (Johnson and Brown, Proc. Nat. Acad. Sci. 1921, 7, 75). 5 : 6-*Dihydrouracil* $C_4H_6O_2N_2$ has m.p. 174°, and sublimes without decomposition at higher temperatures, crystallises in four-sided plates; the *silver* salt $C_4H_5O_2N_2Ag$ is crystalline; the *bromo* derivative $C_4H_5BrO_2N_2$ is a colourless crystalline powder, soluble in 5 parts of hot water, or 10 parts of hot alcohol (Weidel and Roithner, Monatsh. 1896, 17, 172; Tafel, Ber. 1900, 33, 3385; 1901, 34, 144; Fischer and Roeder, *ibid.* 1901, 34, 3751). 4-(*α-ethyloxyethyl*)-2 : 6-*dioxypyrimidine*

$$CO\begin{matrix}<\\<\end{matrix}\begin{matrix}NH{-}CO\\=CH\\NH{-}CCH(CH_3)OC_2H_5\end{matrix}$$

, m.p. 184°–186°, yields dimethylglyoxalone on hydrolysis with aqueous hydrobromic acid (Johnson and Hadley, J. Amer. Chem. Soc. 1916, 38, 1837; 1917, 39, 1715, 2396). 2-*Thiouracil* $C_4H_4ON_2S$ colourless prismatic plates, m.p. 340° with decomposition; 6-*thiouracil* $C_4H_4ON_2S$, small yellow needles, that blacken at 270°, melt and decompose at 328°; 2 : 6-*dithiouracil* $C_4H_4N_2S_2$, thin yellow needles, decomposing above 230° (Wheeler and Liddle, Amer. Chem. J. 1908, 40, 547). *Uracil-4-aldehyde*

$$NH\begin{matrix}<\\<\end{matrix}\begin{matrix}CO\cdot CH\\CO\cdot NH\end{matrix}>C\cdot CHO,H_2O$$

does not melt below 300° (Johnson and Cretcher, J. Amer. Chem. Soc. 1915, 37, 2144). *Uracil-4-carboxylic acid* $NH<^{CO\cdot CH}_{CO\cdot NH}>C\cdot CO_2H,H_2O$, has m.p. 347° (decomp.) (Wheeler, Amer. Chem. J. 1907, 38, 358); becomes anhydrous at 120°, and decomposes above 300° without melting; dissolves in 70 parts of water at 100°; the *amide* $C_5H_5O_3N_3,H_2O$, dissolves in 110 parts of boiling water (Behrend and Struve, Annalen, 1910, 378, 153); the *ethyl ester* is obtained by the condensation of carbamide with ethyl oxalacetate; the *methyl ester* has m.p. 230° (Wheeler, *l.c.*); *uracil-5-carboxylic acid*, colourless prisms, melts and decomposes at 278°; the *methyl ester* forms prisms that decompose at 233° (Wheeler, Johnson and Johns, *ibid.* 1907, 37, 392). *Uracil-3-acetic acid* $HOOC\cdot CH_2N<^{CO\cdot NH}_{CH:CH}>CO$, m.p. 285°, with decomposition; the *methyl ester* has m.p. 216°, the 5-*bromo* derivative melts and decomposes at 244°, the 5-*nitro* derivative melts at 264°–265° with decomposition. *Uracil-4-acetic acid* $NH<^{CO\cdot NH}_{CO\cdot CH}>C\cdot CH_2\cdot CO_2H,H_2O$ has m.p. 340°, is soluble in 8 parts of boiling, or 30 parts of cold water; the *ethyl ester* has m.p. 187°–189°; the *methyl ester* has m.p. 216°–218°; the 5-*nitro* derivative decomposes at 153° (Wheeler and Liddle, Amer. Chem. J. 1908, 30, 1152).

2-*Iminouracil-6-acetic acid*

$$NH<^{CO\text{——}CH}_{C(:NH)\cdot NH}>C\cdot CH_2COOH$$

m.p. 289°-290° (decomp.), decomposes soluble carbonates; its 5-*nitro* derivative decomposes at 309°–310° (Worrall, J. Amer. Chem. Soc. 1918, 40, 1133).

A large number of alkyl and aryl substituted derivatives of uracil have been prepared (Johnson and Derby, Amer. Chem. J. 1908, 40, 444; Fischer and Roeder, Ber. 1901, 34, 3759, 3762; Wheeler and Merriam, Amer. Chem. J. 1903, 29, 490; Wheeler and Bristol, *ibid.* 1905, 33, 448; Johnson and Heyl, *ibid.* 1907, 37, 628; Behrend, Annalen, 1885, 229, 8, 17; 231, 249; Behrend and Roosen, *ibid.* 1889, 251, 238; Behrend and Dietrich, *ibid.* 1889, 309, 260; Behrend and Thurn, *ibid.* 1902, 323, 166; Hagen, 1888, 244, 1; Steudel, Zeitsch. physiol. Chem. 1900, 30, 539; Maizura, Ber. 1908, 41, 176; Johnson and Clapp, J. Biol. Chem. 1908, 5, 49; Johnson and Menge, *ibid.* 1906, 2, 105; Johnson, J. Amer. Chem. Soc. 1914, 36, 1891; Johnson and Matsuo, *ibid.* 1919, 41, 782). The 5-*methyl* derivative or *thymine* is the only one that occurs among the protein degradation products.

Thymine, 5-*methyluracil*, 5-*methyl*-2 : 6-*dioxytetrahydropyrimidine*, $C_5H_6O_2N_2$,

$$CO<^{NH\cdot CO}_{NH\cdot CH}>C\cdot CH_3$$

was discovered by Kossel and Neuman (Ber. 1893, 26, 2753; 1894, 27, 2215) among the products of hydrolysis of the nucleic acid from the thyroid gland; it can be similarly obtained from nucleic acids of other origin (Miescher-Schmiedelberg, Archiv. exp. Path. u. Pharm. 1896, 37, 100; Kossel, Zeitsch. physiol. Chem. 1896, 22, 188; Gulewitsch, *ibid.* 1899, 27, 292; Levene, *ibid.* 1902, 37, 402; 1903, 39, 4, 133, 479; Inouye, *ibid.* 1905, 46, 201; Mandel and Levene, *ibid.* 1905, 46, 155; 1906, 47, 140); and is also formed in the autolysis of the thyroid gland, lymph glands, and pancreas (Kutscher, Zeitsch. physiol. Chem. 1901, 34, 114; Reh, Beitr. chem. Physiol. Path. 1903, 3, 569; Levene, Zeitsch. physiol. Chem. 1905, 45, 498).

Synthesis.—Fischer and Roeder (Ber. 1901, 34, 3751) prepared 5-*methyldihydrouracil* (*hydrothymine*) by the condensation of carbamide with methyl acrylic acid, and the *bromo* derivative of this compound is converted by heating with alkali or pyridine into 5-*methyluracil* or *thymine*. Other methods of synthesis are described by Wheeler and Merriam (Amer. Chem. J. 1903, 29, 478) from ψ-methylthiocarbamide hydriodide and ethyl sodioformylpropionate; and by Gerngross (Ber. 1905, 38, 3394, 3408) from 2 : 4 : 6-trichloro-5-methylpyrimidine obtained from 5-methylbarbituric acid.

For the synthesis of the simplest nucleoside of thymine, namely, 4-hydroxymethyl-5-methyltetrahydropyrimid-2 : 6-dione

$$NH<^{CO\text{—}NH}_{CO\cdot CMe}>C\cdot CH_2\cdot OH$$

m.p. 224°–225° (decomp.), *see* Johnson and Chernoff (J. Amer. Chem. Soc. 1913, 35, 585); and for the synthesis of the *thymine-nucleoside* $NH<^{CO\cdot CMe}_{CO\text{—}NH}>C\cdot CHMe\cdot OH$, m.p. 219°–220°, *v.* Johnson and Hadley (J. Amer. Chem. Soc. 1917, 39, 1919).

Thymine crystallises from water in four-sided plates, or stellate groups of small plates; when carefully heated it sublimes, when heated rapidly it sinters at 318°, and melts with decomposition at 321° (Fischer and Roeder, Ber. 1901, 34, 3758; Steudel, Zeitsch. physiol. Chem. 1900, 30, 539), at 325°–335° (Johnson and Mackenzie, Amer. Chem. J. 1909, 42, 369). Thymine has a bitter taste, it is sparingly soluble in cold, readily soluble in hot water, 100 parts of water at 25° dissolve 0·404 part, and the solution is neutral; it is sparingly soluble in alcohol or ether, and can be recrystallised from concentrated hydriodic or hydrobromic acid.

Salts.—The *potassium* $C_5H_5N_2O_2K,\frac{1}{2}H_2O$ and *sodium* salts $C_5H_5N_2O_2Na$ crystallise from dilute alcohol; the *mercury* salt $C_5H_4N_2O_2Hg$ is a white precipitate; the *lead* salt $C_5H_4N_2O_2Pb,2H_2O$ crystallises in needles (Myers, J. Biol. Chem. 1910, 7, 249).

Derivatives.—4 : 5-*Dihydrothymine*

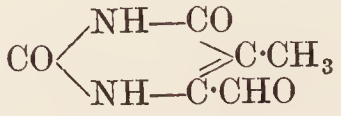
$$CO<^{NH\cdot CO}_{NH\cdot CH_2}>CHMe$$

prepared by the condensation of methyl acrylic acid with carbamide, forms microscopic crystals, m.p. 264°–265° (corr.) (Fischer and Roeder, Ber. 1901, 34, 3758). 4-*Hydroxy* 5-*nitro*-4 : 5-*dihydrothymine* $CO<^{NH\cdot CO\text{——}}_{NH\cdot CH(OH)}>CMeNO_2$, formed by rapid evaporation to dryness of a solution of thymine in fuming nitric acid, crystallises in triclinic prisms, m.p. 183°–185° (α- variety), but sometimes 230°–235° (β- variety); the sparing solubility in alcohol of this compound, as compared with the ready solubility of the nitro-derivative of uracil, forms the basis of a method of separating the two pyrimidines (Johnson,

Amer. Chem. J. 1908, 40, 34; J. Biol. Chem. 1908, 4, 407). *Thymine-4-carboxylic acid*

$$NH<\begin{matrix}CO\cdot CMe\\CO\cdot NH\end{matrix}>C\cdot CO_2H$$

m.p. 328°–330°; the *potassium*, *lead*, and *barium* salts are crystalline; the *ethyl ester* has m.p. 255° (Johnson, J. Biol. Chem. 1907, 3, 299). *Thymine-5′-carboxylic acid* (*thymine-ω-carboxylic acid*) $CO<\begin{matrix}NH\cdot CO\\NH\cdot CH\end{matrix}>C\cdot CH_2\cdot CO_2H$, melts and decomposes at 315°–320°. The *lead* and *potassium* salts are described (Johnson and Speh, Amer. Chem. J. 1907, 38, 602). 4-*Aldehydothymine* (4-*aldehydo*-5-*methyltetrahydropyrimid*-2:6-*dione*)



m.p. 212°–213°, (Johnson and Cretcher, J. Amer. Chem. Soc. 1916, 26, 99).

2-*Thiothymine* $CS<\begin{matrix}NH\cdot CO\\NH\cdot CH\end{matrix}>CMe$, produced by the condensation of thiourea with ethyl sodioformylpropionate, forms crystalline *sodium*, *potassium* and *copper* salts, and is converted quantitatively into thymine by evaporating to dryness an aqueous solution containing a slight excess of chloracetic acid (Wheeler and McFarland, Amer. Chem. J. 1910, 43, 25). 2:6-*Dithiothymine* $C_5H_6N_2S_2$, yellow needles, m.p. 281°, with decomposition; 6-*thiothymine*, yellow silky needles, m.p. 330° (Wheeler and McFarland, *l.c.*).

For the *alkyl* derivatives of thymine, *v.* Johnson and Clapp, J. Biol. Chem. 1908, 5, 49; Steudel, Zeitsch. physiol. Chem. 1900, 30, 539; Wheeler and McFarland, Amer. Chem. J. 1910, 43, 35; Johnson and Derby, *ibid.* 1908, 40, 456, 457. For thymine as soporific, *v.* Hirsch, Deut. med. Wochschr. 39, 2141, from Amer. Chem. Abs. 1914, 374.

Barbituric acid, *malonylcarbamide*, 2:4:6-*trioxyhexahydropyrimidine* $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH_2$ was first obtained by Baeyer (Annalen, 1863, 127, 199; 1864, 130, 136) by reducing with hydrogen iodide or sodium amalgam, the compound (*dibromobarbituric acid*) prepared by the action of bromine on violuric or dilituric acid. It can be prepared by the reducing action of warm concentrated sulphuric acid on alloxantin (Finck, *ibid.* 1864, 132, 304); or synthetically by the condensation of malonic acid with carbamide in the presence of phosphoryl chloride (Grimaux, Bull. Soc. chim. 1879, [ii.] 31, 146); or acetic anhydride (Biltz and Wittek, Ber. 1921, 54, 1035); or of ethyl sodiomalonate with carbamide in alcoholic solution (Michael, J. pr. Chem. 1887, [ii.] 35, 456). Barbituric acid has also been prepared by the action of hot mineral or acetic or formic acid on the iminobarbituric acid obtained by the condensation of carbamide with ethyl cyanacetate in the presence of sodium ethoxide (Conrad, Annalen, 1905, 340, 310); or similarly from the *di-iminobarbituric acid* obtained from malononitrile and carbamide (Merck, D. R. P. 166448); or the *tri-iminobarbituric acid* obtained by the condensation of malononitrile with guanidine (Merck, D. R. PP. 165692, 165693); or by the condensation of ethyl malonamate with urethane (Chemische Fabrik auf Aktien, vorm. E. Schering, D. R. P. 171294); or by the action of alkaline condensing agents on the ureides of the half-acid esters of malonic acid

$$RO_2C\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot NH_2$$

(Boehringer and Sohne, D. R. P. 193447); or by the action of ammonia on malonyl diurethane (Conrad and Schulze, Ber. 1909, 42, 729).

Barbituric acid crystallises in large colourless prisms containing $2H_2O$, becomes anhydrous in the desiccator, and decomposes on melting at 253° (Maquenne block); it is a dibasic acid forming normal and acid salts, the acidic constant $ka = 10{\cdot}51\times10^{-5}$ (Wood, Chem. Soc. Trans. 1906, 1835), and the salts have the constitution represented by the formula $CO<\begin{matrix}NH\cdot C(OM)\\NH\cdot CO\text{——}\end{matrix}>CH$ (Wood and Anderson, *ibid.* 1909, 979); the *ammonium* $C_4H_3O_3N_2(NH_4)$, *potassium* $C_4H_3O_3N_2K$, *sodium* $C_4H_3O_3N_2Na$ and $C_4H_2O_3N_2Na_2,2H_2O$, *barium*

$$(C_4H_3O_3N_2)_2Ba,2H_2O$$

copper $(C_4H_3O_3N_2)Cu,3H_2O$, and *lead*

$$C_4H_2O_3N_2Pb$$

salts are crystalline (Baeyer, Annalen, 1864, 130, 141); *cf.* Biltz (Annalen, 1914, 404, 186). For morphine barbituric acids, useful as sedatives, *v.* Eng. Pat. 107409.

For the physiological action of pyrimidines of the barbituric acid series, *v.* Kleiner, J. Biol. Chem. 1912, 11, 443.

1-*Methylbarbituric acid* $CO<\begin{matrix}NMe\cdot CO\\NH\cdot CO\end{matrix}>CH_2$ has m.p. 133° (Conrad, Annalen, 1905, 340, 310); 1:3-*dimethylbarbituric acid* crystallises in flattened needles (Mulder, Ber. 1879, 12, 465; Techow, *ibid.* 1894, 27, 3082); 1:3-*diethylbarbituric acid* has m.p. 52°–53° (Sembritzki, *ibid.* 1897, 30, 1814); and 1:3-*diphenylbarbituric acid* has m.p. 238° (Whiteley, Chem. Soc. Trans. 1907, 91, 1339).

For compounds of dialkyl barbituric acids and quinine derivatives, *v.* Merck, D. R. P. 291421.

Ether-like derivatives of barbituric acid, prepared by the usual methods from aryl- or alkyl-aryloxyalkyl malonic acid, containing at least one aryl residue attached to an oxygen atom, possess strong hypnotic action combined with low toxic effects, Farbenfabriken vorm. F. Bayer & Co., D. R. P. 295492, from J. Soc. Chem. Ind. 1917, 36, 306.

The methylene group situated between two CO groups in barbituric acid and in its 1- and 1:3- substituted derivatives $CO<\begin{matrix}NR\cdot CO\\NR\cdot CO\end{matrix}>CH_2$ is highly reactive, and the hydrogen atoms can be replaced by: (1) acyl groups forming the *acyl barbituric acids* (*v. infra*); (2) halogens yielding the halogen derivatives of barbituric acid (*v. infra*); (3) hydroxyl yielding the *dialuric acids* $CO[NR\cdot CO]_2CH\cdot OH$ and the *alloxan* $CO[NR\cdot CO]_2C(OH)_2$ or $CO[NR\cdot CO]_2CO$ (*q.v.*); (4) a nitro group, yielding the *dilituric acids* $CO[NR\cdot CO]_2CH\cdot NO_2$ (*q.v.*); (5) a *nitroso group* forming the iso*nitroso barbituric acids* or violuric acids $CO[NR\cdot CO]_2C:NOH$ (*v. infra*); (6) the amino group yielding the *uramil* (*murexan*) $CO[NR\cdot CO]_2CH\cdot NH_2$ (*v. infra*), of which the sulphamino derivative is *thionuric acid*

$$CO[NR\cdot CO]_2CH\cdot NHSO_3H$$

(*v. infra*), and the carbamido derivative is *ψ-uric acid* $CO[NR{\cdot}CO]_2CH{\cdot}NH{\cdot}CO{\cdot}NH_2$ (*v. infra*); (7) alkyl groups, forming the 5- or C-*mono*-, and 5 : 5- or CC-*di-alkylbarbituric acids* $CO[NR{\cdot}CO]_2CHR'$ and $CO[NR{\cdot}CO]_2CR'R''$ (*v. infra*).

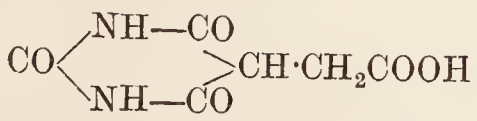
Barbituric acid and its 1- or 1 : 3- substituted derivatives also condense with aldehydes to form derivatives of the type $CO[NR{\cdot}CO]_2C : CHR'$ (*v. infra*), and with aromatic diazonium salts to form *hydrazones* $CO[NR{\cdot}CO]_2C : N{\cdot}NHR'$, and *azo* compounds $CO[NR{\cdot}CO]_2CR'N : NR''$(*v.* ALLOXAN, and *infra*).

Acyl derivatives of barbituric acid. The acyl derivatives of barbituric acid and its 1 : 3- substituted derivatives have the constitution represented by the formula

$$CO<\begin{matrix}NR{\cdot}CO\\NR{\cdot}CO\end{matrix}>CH{\cdot}COR$$

and have the usual properties of ketones, yielding *oximes* and *hydrazones* (Biltz and Wittek, Ber. 1921, 54, 1035). The acetyl derivative of barbituric acid and of its 1 : 3-substituted derivatives occur as bye-products in the synthetic formation of the acid from malonic acid and the carbamide in the presence of phosphoryl chloride. 5-*Acetylbarbituric acid* forms colourless crystalline needles, m.p. 296°–300° (decomp.) (Grimaux, Compt. rend. 1878, 87, 752; 1879, 88, 85; Conrad and Guthzeit, Ber. 1882, 15, 2844; Biltz and Wittek); 5-*acetyl*-1-*methylbarbituric acid*, m.p. 207° (decomp.); 5-*acetyl*-1 : 3-*dimethylbarbituric acid*, m.p. 195°; 5-*acetyl*-1-*ethylbarbituric acid*, m.p. 162°–163°; Biltz and Wittek (*l.c.*); 1 : 3-*diethylacetylbarbituric acid* $C_8H_4N_2O_3Ac$ has m.p. 62·5° (Sembritzki, *ibid.* 1897, 30, 1814); 1 : 3-*diphenylacetylbarbituric acid* $C_{16}H_{11}O_3N_2Ac$, obtained as a bye-product in the synthetic preparation of 1 : 3-diphenylbarbituric acid, also prepared by the action of acetyl chloride on the sodium salt of 1 : 3-diphenylbarbituric acid, has m.p. 150°, and forms a sparingly soluble sodium salt; 1 : 3-*diphenyl*-5-*ethylacetylbarbituric acid*, obtained by the action of ethyl iodide and silver oxide on the preceding compound, has m.p. 139°. 1 : 3-*Diphenylbenzoylbarbituric acid* $C_{16}H_{11}O_3N_2Bz$ prepared from benzoyl chloride and the sodium derivative of 1 : 3-diphenyl barbituric acid, has m.p. 228°; the 5-*methyl* derivative has m.p. 158°, the 5-*ethyl* derivative has m.p. 243°, and the 5-*bromo* derivative melts at 186°, and is reduced to the benzoyl compound by hydrogen iodide with the liberation of one molecular proportion of iodine (Whiteley and Judd, private communication; Backes, West and Whiteley, Chem. Soc. Trans. 1921, 119, 378).

Barbituryl-5-*acetic acid*



chars at 230° and decomposes at 250° (Johnson and Kohmann, Amer. Chem. J. 1913, 49, 192).

Halogen derivatives of barbituric acid. *Bromo derivatives.*—The 5-mono- and 5 : 5-di-bromo derivatives of barbituric acid and its 1 : 3-substituted derivatives are reduced by hydrogen iodide, forming barbituric acid, and liberating iodine according to the equation

$$CO[NR{\cdot}CO]_2CBr_2+4HI = CO[NR{\cdot}CO]_2CH_2+2HBr+2I_2$$

the reaction is quantitative, takes place rapidly at the ordinary temperature, and affords a ready method of analysis (Backes, West and Whiteley, *l.c.*).

5-*Bromobarbituric acid* $CO[NH{\cdot}CO]_2CHBr$, prepared by reducing the dibromo derivative with sodium amalgam or zinc-dust, or by heating it with aqueous prussic acid, forms small needles, sparingly soluble in water (Baeyer, Annalen, 1864, 130, 134). 5-*Bromobarbituric acid* $CO[NH{\cdot}CO]_2CHBr{\cdot}2H_2O$, prepared by treating 5 : 5-dibromobarbituric acid with concentrated ammonia solution, transforming the ammonium monobrombarbiturate into the sodium salt and boiling this with 40 p.c. sulphuric acid, has m.p. 210°–216° (decomp.) (Biltz and Hamburger, Ber. 1916, 49, 635). 5 : 5-*Dibromobarbituric acid* $CO[NH{\cdot}CO]_2CBr_2$, prepared by the action of bromine on barbituric, violuric, dilituric, or hydurilic acid (Baeyer, Annalen, 1863, 127, 229), or by oxidising dibromo-oxymethyluracil with fuming nitric acid (Behrend, *ibid.* 1886, 236, 62), forms sparingly soluble rhombic crystals, m.p. 234° (decomp.). 5-*Bromo*-5-*methylbarbituric acid* has m.p. 192·5° (corr.) (Fischer and Dilthey, *ibid.* 1904, 335, 334). 1-*Methyl*-5-*bromo-barbituric acid*, m.p. 105°–106°. 1-*Methyl*-5 : 5-*dibromo-barbituric acid*, m.p. 98°–99° (Biltz and Hamburger, Ber. 1916, 49, 635).

1 : 3-*Diethyl*-5-*bromobarbituric acid*, m.p. 81°–82° (Biltz and Hamburger, *l.c.*). 1 : 3-*Diethyl*-5 : 5-*dibromobarbituric acid* $CO[NEt{\cdot}CO]_2CBr_2$, has m.p. 86°–87° (corr.) (Sembritzki, Ber. 1897, 30, 1814). 1 : 3-*Diphenyl*-5-*bromobarbituric acid* $CO[NPh{\cdot}CO]_2CHBr$ has m.p. 155° (Backes, West and Whiteley, *l.c.*). 1 : 3-*Diphenyl*-5 : 5 -*dibromobarbituric acid* $CO[NPh{\cdot}CO]CBr_2,C_6H_6$, m.p. 152°; the benzene-free compound has m.p. 160° (Whiteley, Chem. Soc. Trans. 1907, 91, 1347); 5 - *bromo* - 1 : 3-*diphenylbenzoylbarbituric acid* has m.p. 186° (Whiteley, Chem. Soc. Proc. 1908, 24, 288).

Chloro derivatives.—5-*Chlorobarbituric acid* decomposes at 280° (Biltz and Hamburger, *l.c.*). 5 : 5-*Dichlorobarbituric acid*, obtained by the oxidation of dichloro-oxymethyluracil, crystallises in prisms or plates, $a : b : c = 0{\cdot}7766 : 1 : 0{\cdot}8929$ (Behrend, Annalen, 1886, 236, 57), m.p. 219°–220° (Biltz and Hamburger, *l.c.*). 5-*Chloro*-1-*methylbarbituric acid* crystallises in quadratic tables with one molecule of water, m.p. 137°. 5-*Chloro*-1 : 3-*dimethylbarbituric acid* crystallises with one molecule of water, m.p. 129° (Biltz and Hamburger, *l.c.*). 5 : 5-*Dichloro*-1 : 3-*dimethylbarbituric acid*, obtained by treating amalic acid (tetramethylalloxantin) with phosphoric chloride, has m.p. 157° (Techow, Ber. 1894, 27, 3082). 5 : 5-*Dichloro*-1 : 3-*diethylbarbituric acid* has m.p. 85·7 (corr.) (Sembritzki, *ibid.* 1879, 30, 1814).

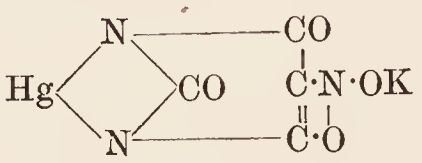
***iso*Nitroso derivatives of barbituric acids. Violuric acids.** Violuric acid or *iso*nitrosobarbituric acid is so called because, although colourless in the solid state, and forming colourless alkyl ethers, it shows a violet colour in solution in pure water, and gives rise to intensely coloured (red, violet, blue, green, and yellow) salts with metals and substituted ammonias (Wagner, Zeitsch. physikal. Chem. 12, 314; Guinchard, Ber. 1899, 32, 1723; Donnan and Schneider, Chem. Soc. Trans. 1909, 95, 956; Zerewitinoff, Ber. 1909, 42, 4802). Hantzsch and his pupils have shown that polychromatism

and chromotropism are exhibited by some of the violurates, and they are of opinion that the violuric acids and their colourless ethers are the true oximino ketones $CO<^{NR\cdot CO}_{NR\cdot CO}>C:NOH$, whilst the *blue* violurates are the nitroso-enolic salts $CO<^{NR\cdot CO-}_{NR\cdot C(OM)}>C\cdot NO$, and the more positive the nature of the metallic radicle present and the solvent, the more completely are the violuric acids as true oximino-ketones transformed into the structurally isomeric nitroso-enols (Ber. 1899, 32, 575; Guinchard *ibid.* 1723; 1909, 42, 966; 986, 1000; 1910, 43, 45; 82). Another explanation of the differences in constitution between the colourless violuric acids and the coloured violurates is to regard the latter as derivatives of the oxime

$$CO<^{NH\cdot CO}_{NH\cdot CO}>C:NOH$$

whilst the colourless acids are *iso*-oximes $CO<^{NH.CO}_{NH\cdot CO}>C<^{NH}_{O}$ (Lowry, Brit. Assoc. Reports, 1904, 222; Hartley, Chem. Soc. Trans. 1905, 87, 1816; Baly, *ibid.* 1906, 89, 981; Whiteley, *ibid.* 1907, 91, 1331).

Violuric acid $CO[NH\cdot CO]_2C:NOH,H_2O$, prepared by the action of nitrous acid or nitric acid (sp.gr. 1·2) on hydurilic acid (Baeyer, Annalen, 1863, 127, 200); by treating barbituric acid with potassium nitrite (Baeyer, *ibid.* 1864, 130, 140); by heating dilituric acid with glycerol, or by warming its iron salt with potassium cyanide; or by the action of hydroxylamine hydrochloride on alloxan (Ceresole, Ber. 1883, 16, 1133; Pellizzari, Gazz. chim. ital. 1887, 17, 258), is a monobasic acid, and decomposes acetates; it also yields a pale flesh-coloured *mercuric* derivative, the potassium salt



of which is deep violet, becoming blue when anhydrous (Auld, Chem. Soc. Trans. 1907, 91, 1047). The *methyl ether* $C_4H_2O_3N_3.CH_3$ is colourless, and has m.p. 270° (Guinchard, Ber. 1899, 32, 1723); the *benzyl ether* $C_4H_2O_3N_3\cdot C_7H_7$ is also colourless, and has m.p. 222° (Hantzsch and Isherwood, *ibid.* 1909, 42, 986).

1-*Methylvioluric acid* $C_5H_5O_4N_3,H_2O$ decomposes carbonates and acetates (Andreasch, Monatsh. 1900, 21, 281); it has m.p. 202°–203° (Biltz and Hamburger, *l.c.*). 1 : 3-*Dimethylvioluric acid* $CO[NMe\cdot CO]_2C:N\cdot OH,H_2O$ has m.p. 124°, the anhydrous substance melts at 141° (Techow, Ber. 1894, 27, 3084; Andreasch, Monatsh. 16, 17; Whiteley, Chem. Soc. Trans. 1903, 83, 19); the benzyl ether $C_{13}H_{13}O_4N_3$ has m.p. 164° (Hantzsch and Isherwood, *l.c.*). 1 : 3-*Diethylvioluric acid* $CO[NEt\cdot CO]_2C:NOH,H_2O$ melts at 90° and loses H_2O at 107° (Sembritzki, Ber. 1897, 30, 1814). 1 : 3-*Diphenylvioluric acid* $CO[NPh\cdot CO]_2C:N\cdot OH$ has m.p. 227°; the *acetyl* derivative $C_{16}H_{10}O_4N_3Ac$ melts and decomposes at 245° (Whiteley, Chem. Soc. Trans. 1907, 91, 1339).

Amino derivatives of barbituric acids. *Uramil* (*murexan*), 5-*amino*-2 : 4 : 6-*trioxyhexahydropyrimidine* $CO<^{NH\cdot CO}_{NH\cdot CO}>CH\cdot NH_2$, was originally prepared by boiling alloxantin with ammonium chloride or ammonium thionurate with hydrochloric acid (Liebig and Wöhler, Annalen, 1838, 26, 310); it is formed together with alloxan and ammonia when murexide is decomposed by acids (Beilstein, Annalen, 1858, 107, 183), or by caustic alkalis (Reoch, Chem. News, 1875, 32, 171); and is obtained when alloxanphenylhydrazone is reduced with tin and hydrochloric acid (Kühling, Ber. 1898, 31, 1973). Uramil is conveniently prepared by reducing nitro- or nitrosobarbituric acid with hydriodic acid (Baeyer, Annalen, 1863, 127, 223); or by heating ammonium dialurate, closed vessels being employed to avoid oxidation (Piloty and Finckh, *ibid.* 1900, 333, 71). Uramil forms silky needles, insoluble in cold, sparingly soluble in hot water, it gives murexide on long boiling with ammonia; it has heat of combustion +380 Cal., and heat of formation +170·7 Cal. (Matignon, Ann. Chim. [vi.] 28, 289). Uramil forms metallic derivatives in which the iminohydrogen atoms are replaced by metals, *potassium uramil* $CO[NK\cdot CO]_2CH\cdot NH_2,2H_2O$, obtained in slender pale yellow needles by dissolving uramil in warm 50 p.c. potassium hydroxide solution, is converted by iodine into potassium murexide, and by methyl iodide into 1 : 3-dimethyluramil; the *acid potassium salt* $C_4H_5O_3N_3,C_4H_4O_3N_3K$ forms colourless sparingly soluble leaflets; the *barium* and *lead* salts have also been prepared. 7-*Acetyluramil* forms crystalline salts, of which the *potassium*, *ammonium*, *silver*, *barium*, *lead*, and *copper* salts are described. 7-*Methyluramil* $CO[NH\cdot CO]CH\cdot NHMe$ is prepared from alloxantin and methylamine acetate; the *ethyl* derivative $C_4H_4N_3O_3Et$ is similarly prepared (Piloty and Finckh, Annalen, 1900, 333, 71; *cf.* Fischer, Ber. 1897, 30, 561). 5-*Methyluramil*

$$CO[NH\cdot CO]_2CMe\cdot NH_2$$

m.p. 237° (corr.) is prepared by treating 5-bromo-5-methylbarbituric acid with alcoholic ammonia; 5-*ethyluramil* has m.p. 216° (corr.) (Fischer and Dilthey, Annalen, 1904, 335, 334). 1-*Methyl-uramil* is prepared from methylalloxan and ammonium sulphite (Fischer, Ber. 1897, 30, 3091). 1 : 3-*Dimethyluramil*

$$CO[NMe\cdot CO]_2CH\cdot NH_2$$

decomposes at 200° (Techow, *ibid.* 1894, 27, 3087). 1 : 3 : 7-*Trimethyluramil* decomposes at 200° (Fischer, *ibid.* 1897, 30, 559). 1 : 3-*Diethyluramil* decomposes at 200° (Sembritzki, *ibid.* 1897, 30, 1814). 1 : 3-*Diphenyluramil*, m.p. 97°, forms a crystalline hydriodide readily soluble in cold water, with dissociation into hydrogen iodide and the uramil (Whiteley, Chem. Soc. Trans. 1907, 91, 1340); *v.* Fiorc (Boll. chim. farm. 1915, 54, 449) for attempts to obtain 1-*amino* derivatives of alkylbarbituric acids.

Thionuric acid. *Sulphaminobarbituric acid* $CO[NH\cdot CO]_2CH\cdot NH\cdot SO_3H,1\frac{1}{2}H_2O$ is prepared by heating alloxan or violuric acid with a solution of ammonium sulphite (Liebig and Wöhler, Annalen, 1838, 26, 268; Baeyer, *ibid.* 1863, 127, 210). The free acid, obtained by decomposing the lead salt with sulphuretted hydrogen is a crystalline mass, readily soluble in water, forming a strongly acid solution; it is a dibasic

acid yielding acid and normal salts, and is hydrolysed on boiling with water, yielding uramil and sulphuric acid. 1 : 3-*Dimethylthionuric acid* is obtained as its ammonium salt

$$CO[NMe\cdot CO]_2CH\cdot NH\cdot SO_3NH_4,2H_2O$$

by heating at 100° a solution of 1 : 3-dimethylalloxan with ammonium sulphite and ammonium bicarbonate (Techow, Ber. 1894, 27, 3086), the salt loses $2H_2O$ at 105°, and decomposes at 180°; the *barium salt* $C_6H_7N_3O_6SBa$ is also described. The *dimethylamine salt*

$$CO<\begin{matrix}NH\text{———}CO\\N(NHMe_2)\cdot CO\end{matrix}>C(OH)\cdot SO_3\cdot NH_2Me_2$$

is obtained when alloxan is treated in aqueous solution with a neutral solution of dimethylamine sulphite, it is decomposed by dilute acids yielding sulphur dioxide, alloxantin, and dimethylamine, but no trace of substituted uramil (Piloty and Finckh, Annalen, 1904, 333, 71).

ψ-Uric acid, *carbamidobarbituric acid*

$$CO[NH\cdot CO]_2CH\cdot NH\cdot CO\cdot NH_2$$

prepared by boiling aminobarbituric acid with potassium cyanate (Baeyer, *ibid.* 1863, 127, 3), or heating it with carbamide at 180° (Grimaux, Bull. Soc. chim. 1879, [ii.] 31, 535), forms prisms, sparingly soluble in cold water, and is converted by fusing with anhydrous oxalic acid, or by boiling with 25 p.c. hydrochloric acid, into uric acid. Pseudouric acid is a monobasic acid, and the *ammonium* $C_5H_5N_4O_4NH_4,H_2O$; *potassium* $C_5H_5N_4O_4K,H_2O$; *sodium*

$$C_5H_5N_4O_4Na,2H_2O$$

barium $(C_5H_5N_4O_4)_2Ba,5H_2O$; *calcium*; *lead* $(C_5H_5N_4O_4)_2Pb,2H_2O$; *copper* and *mercury* salts are crystalline. 7-*Methylpseudouric acid* $CO[NH\cdot CO]_2CH\cdot NMe\cdot CO\cdot NH_2$ is prepared from 7-methyluramil and potassium cyanate (Fischer, Ber. 1897, 30, 562). 1 : 3-*Dimethylpseudouric acid* $CO[NMe\cdot CO]_2CH\cdot NH\cdot CO\cdot NH_2$ has m.p. 210° (Techow, *ibid.* 1894, 27, 3088). 1 : 3 : 7-*Trimethylpseudouric acid* decomposes between 180° and 190°, when slowly, and at 195° when rapidly heated (Fischer, *l.c.*). 1 : 3-*Diethylpseudouric acid* has m.p. 196° (corr.) with decomposition (Sembritzki, *ibid.* 1897, 30, 1823). 1 : 3-*Diphenylpseudouric acid* melts and decomposes at 217° (Whiteley, Chem. Soc. Trans. 1907, 91, 1341). 4-*Amino-ψ-uric acid* crystallises from hot water with $1H_2O$ in oblong plates (Levene and Senior, J. Biol. Chem. 1916, 25, 607).

2-*Thio-ψ-uric acid*, colourless crystalline powder, when hydrated, turns purple when dehydrated, decomposes above 300° (Johnson and Nicolet, J. Amer. Chem. Soc. 1914, 36, 345).

5-*Methoxy-ψ-uric acid*, m.p. 202°–204° (decomp.); 5-*chloro-ψ-uric acid*, m.p. 125° (decomp.); 5-*ethoxy-ψ-uric acid*, m.p. 227°–228° (decomp.); 5-*hydroxy-ψ-uric acid*, m.p. 210° (decomp.), reacts with bases to give the corresponding 5-*amino-ψ-uric acid*, of which the following have been prepared: *amino-*, m.p. 145°–147° (decomp.), *methylamino-*, m.p. 191°–192° (decomp.), *ethylamino-*, m.p. 170°–171° *dimethylamino-*, m.p. 191°–192° (decomp.), *diethylamino-*, m.p. 163°–165° (decomp.), and *anilino-*, m.p. 194°–196° (decomp.), and these on reduction yield the corresponding 7-*alkyl-* or 7 : 7 *dialkyl-uramils* (Biltz and Heyn, Annalen, 1916, 413, 7).

5-Mono- and 5 : 5-Di-alkyl derivatives of barbituric acid. The following general methods have been employed for the preparation of the 5-mono- and 5 : 5-di-alkyl barbituric acids, or as they are sometimes called the C-alkyl or CC-dialkyl-barbituric acids: (1) Direct alkylation of the barbituric acid by the action of the alkyl halide on the silver salt (Conrad and Guthzeit, Ber. 1881, 14, 1643; 1882, 15, 2844; Gebrüder von Niessen, D. R. P. 144432). (2) Condensation of the *ethyl ester* of the *alkyl malonic acid* with (*a*) *carbamide* in the presence of sodium ethoxide, the alkali metal or its amide (Merck, D. R. PP. 146948, 147278, 147279, 147280; Fischer and Dilthey, Annalen, 1904, 335, 334); (*b*) *biuret* or *alkyl allophanate* (Merck, D. R. P. 183857); (*c*) *carbamide* in the presence of alkali or alkaline earth carbides (Merck, D. R. P. 185963); (*d*) *guanidine* and subsequent hydrolysis of the 2-iminobarbituric acid obtained (Chemische Fabrik auf Aktien, vorm. E. Schering, D. R. P. 189076). (3) Condensation of *alkyl malonyl chloride* with (*a*) *carbamide* (Merck, D. R. P. 146949); (*b*) *guanidine* and subsequent hydrolysis with dilute acid of the 2-iminobarbituric acid obtained (Merck, D. R. P. 158890); (*c*) *urethane* and the conversion of the diurethanes into the barbituric acid by heating with alkyl oxides, hydroxides or fuming mineral acids (Traube, D. R. PP. 171992, 172885, 172886); (*d*) with *alkyl allophanates* (Merck, D. R. P. 177694). (4) Condensation of the *alkyl malonitrile* with: (*a*) *guanidine* and subsequent hydrolysis of the 2 : 4 : 6-tri-iminobarbituric acid thus obtained (Merck, D. R. PP. 165692, 165693); (*b*) *carbamide, thiocarbamide* or *guanidine* in the presence of the carbides of the alkali or alkali earth metals (Merck, D. R. P. 185963). (5) Condensation of *dialkylmalonamides* with (*a*) *alkyl carbonates* in the presence of alkali ethoxides (Farbenfabriken vorm. Friedr. Bayer & Co., D. R. PP. 163136, 168406, 168407); (*b*) *oxalyl chloride* (Einhorn, D. R. P. 225457). (6) By the action of acid condensing agents on the tetra-substituted diureides of the dialkylmalonic acids $CX_2(CO\cdot NH\cdot CO\cdot NR_2)_2$ (Einhorn, D. R. P. 193446). (7) By the action of alkali condensing agents on the ureides of the half acid esters of alkylmalonic acids

$$NH_2\cdot CO\cdot NH\cdot CO\cdot CRR'\cdot CO_2R''$$

(Boehringer and Söhne, D. R. P. 193447). (8) Condensation of *ethyl dialkylcyanacetate* with: (*a*) *carbamide* in the presence of sodium ethoxide, and subsequent hydrolysis of the 4-iminobarbituric acid thus obtained (Merck, D. R. PP. 156384, 156385); (*b*) *carbamide* or *thiocarbamide* and subsequent hydrolysis of the imino or thio-iminobarbituric acid thus obtained by heating with mineral, formic, or acetic acids (Conrad, Annalen, 1905, 340, 310); (*c*) *guanidine* in the presence of various condensing agents, and subsequent hydrolysis of the 2 : 4-di-iminobarbituric acid thus obtained (Farbenfabriken vorm. Friedr. Bayer & Co., D. R. P. 158592; Chemische Fabrik auf Aktien, vorm. E. Schering, D. R. P. 201244; Basler Chemische Fabrik, D. R. P. 204795; (*d*) *dicyanodiamides* in the presence of alkali condensing agents and subsequent hydrolysis of the substituted barbituric acid thus obtained (Farbenfabriken vorm. Friedr. Bayer & Co., D. R. P. 165223); (*e*)

carbamide, *thiocarbamide*, or *guanidine* in the presence of the carbides of the alkali or alkali earth metals (Merck, D. R. P. 185963).

The following 5-substituted alkyl derivatives of barbituric acid are described: the 5-*methyl*, m.p. 202°–203° (Fischer and Dilthey, Annalen, 1904, 335, 334); the 5-*ethyl*, m.p. 194° (Merck, D. R. P. 165693); the 5-*propyl*, m.p. 207°–208°; the 5-iso*propyl*, m.p. 216°; the 5-*allyl*, m.p. 167° (Johnson and Hill, Amer. Chem. J. 1911, 46, 537); the 5-*benzyl*, m.p. 206° (Conrad and Guthzeit, Ber. 1882, 15, 2844); the 5 : 5-*dimethyl*, m.p. 279°; the 5-*methyl*-5-*ethyl*, m.p. 212°; the 5-*methyl*-5-*propyl*, m.p. 182°; the 5 : 5-*diethyl* or *veronal*, m.p. 191° (corr.) (*q.v.* and SYNTHETIC DRUGS); the 5 : 5-*diallyl*, m.p. 173° (Johnson and Hill, *l.c.*); the 1-*methyl*-5 : 5-*diethyl*, m.p. 154·5°; the 1-*phenyl*-5 : 5-*diethyl*, m.p. 197°; the 1 : 3 : 5 : 5-*tetraethyl*, b.p. 125·5°–126°/8·8 mm.; the 5-*ethyl*-5-*propyl*, m.p. 146°; the 5 : 5-*dipropyl* or *proponal*, m.p. 146° (Fischer and Dilthey, *l.c.*; Merck, D. R. P. 156385), 166° (Conrad, Annalen, 1905, 340, 310) (*v.* SYNTHETIC DRUGS); the 5 : 5-*di*-iso*butyl*, m.p. 173·5°; the 5 : 5-*di*-iso*amyl*, m.p. 172°; the 5 : 5-*di*-*benzyl*, m.p. 222° (Fischer and Dilthey, *l.c.*); the 5-*benzyl*-5-*allyl*, m.p. 198° (Johnson and Hill, *l.c.*).

For the 5 : 5-unsymmetrical disubstituted alkylaryl derivatives, *v.* Farbenfabriken vorm. F. Bayer & Co., D. R. PP. 249722, 293163; for the 5 : 5-alkylalkoxyalkyl derivatives, *v.* Chem. Werke vorm. Byk, D. R. P. 285636; for *di-alkylethylene* derivatives, *v.* Wolff, D. R. P. 233968; and for *di-alkylthio-* barbituric acids, *v.* Merck, D. R. P. 234012.

Condensation of barbituric acids with aldehydes and ketones. Barbituric acid and its 1- and 1 : 3-substituted derivatives condense readily, in the absence of condensing agents, with aldehydes or with dichloroketones to form alkylidene derivatives of the types

$$CO[NH\cdot CO]_2C : CHR \text{ and}$$

$CO[NH\cdot CO]_2C : CRR'$, which on reduction yield the corresponding 5-alkylbarbituric acids

$$CO[NH\cdot CO]_2CH\cdot CH_2R \text{ and}$$

$CO[NH\cdot CO]_2CH\cdot CHRR'$. These compounds are usually sparingly soluble, and barituric acid and thiobarbituric acid can be used as quantitative precipitants for furfuraldehyde (Dox and Plaisance, J. Amer. Chem. Soc. 1916, 38, 2156). 5-*Benzylidenebarbituric acid* $CO[NH\cdot CO]_2C : CHPh$, m.p. 256°; and o-*nitrobenzylidenebarbituric acid*, m.p. 250°–252°, are colourless; *cinnamylidenebarbituric acid*, m.p. 226°–228°, and *furfurylidenebarbituric acid*, m.p. above 280°, are yellow (Conrad and Reinbach, Ber. 1901, 34, 1339); p-*hydroxybenzylidenebarbituric acid*, m.p. 300°, is canary-yellow, and p-*dimethylaminobenzylidenebarbituric acid*, m.p. 282°, is orange-red (Weinschenk, *ibid.* 1685).

For the condensation products of thiobarbituric acid with aromatic aldehydes, *see* Dox and Plaisance (*l.c.*); and for the use of thiobarbituric acid as a qualitative test for ketohexose, *see* Plaisance (J. Biol. Chem. 1917, 29, 207).

1 : 3-*Diphenyl*-5-*benzylidenebarbituric acid* $CO[NPh\cdot CO]_2C : CHPh$ exists in two forms, the stable form being yellow, and the labile form being colourless, each melts at 214°; 1 : 3-*diphenyl*-5-*cinnamylidenebarbituric acid*

$$CO[NPh\cdot CO]_2C : CH\cdot CH : CHPh$$

m.p. 268°, is orange-yellow; 1 : 3-*diphenyl*-5-*diphenylmethylenebarbituric acid*

$$CO[NPh\cdot CO]_2C : CPh_2$$

m.p. 264°, is deep yellow. Each of the compounds described above contains the complex $\begin{matrix}\cdot CO\\ \cdot CO\end{matrix}\!>\!C:CRR'$, consisting of three chromophores, yet each is coloured or colourless according to the nature of the radicles R and R'. It would seem that when R is hydrogen and R' phenyl or its ortho- substituted derivative the compound is usually colourless, but that it is yellow when R' is a para- substituted derivative of phenyl, or a more highly unsaturated radicle such as that afforded by cinnamaldehyde or furfuraldehyde; when both R and R' are phenyl groups the compound is also yellow (Whiteley, Chem. Soc. Trans. 1907, 91, 1332).

Condensation of barbituric acids with aromatic diazonium chlorides. Barbituric acid and its 1 : 3-substituted derivatives condense readily with aromatic diazonium salts to form the aryl hydrazone of the corresponding alloxan, the same compound being obtained by the condensation of the arylhydrazine with the corresponding alloxan, or the 5 : 5-dibromo-derivative of the barbituric acid

$$\left.\begin{matrix}CO[NH\cdot CO]_2CH_2 + ClN : NPh \\ CO[NH\cdot CO]_2CO + H_2N\cdot NHPh \\ CO[NH\cdot CO]_2CBr_2 + H_2N\cdot NHPh\end{matrix}\right\rangle \rightarrow CO[NH\cdot CO]_2C : N\cdot NHPh$$

(*v.* ALLOXAN).

When 5-substituted derivatives of barbituric acid condense with aromatic diazonium salts the products are azo compounds of the type $CO[NR\cdot CO]_2CR'N : NR''$, these are readily hydrolysed by mineral acids yielding nitrogen, and the phenol corresponding with the aromatic diazonium salt, and regenerating the barbituric acid

$$CO[NR\cdot CO]_2CR'N : NR'' \rightarrow CO[NR\cdot CO]_2CHR' + N_2 + R''OH$$

5-*Benzeneazo*-1:3-*diphenyl*-5-*benzylbarbituric acid* $CO[NPhH\cdot CO]_2C(CH_2Ph)\cdot N : NPh$, m.p. 170°–171°, forms bright yellow prisms; the p-*nitro* derivative crystallises in bright yellow prisms, m.p. 181°–182°; 5-*benzeneazo*-1 : 3-*diphenyl*-5-*diphenylmethylbarbituric acid*

$$CO[NPh\cdot CO]_2C(CHPh_2)\cdot N : NPh$$

bright yellow prisms, m.p. 160°; the p-*nitro* derivative forms canary-yellow prisms, m.p. 175° (Whiteley, Chem. Soc. Trans. 1907, 91, 1344).

***iso*Barbituric acid**, 5-*hydroxyuracil*

$$CO\!<\!\begin{matrix}NH\cdot CH\\ NH\cdot CO\end{matrix}\!>\!C\cdot OH$$

is one of the products obtained by the reduction of nitrouracil; it forms an *acetyl* derivative, and when treated with bromine water yields *iso*-dialuric acid (*q.v.*) (Behrend and Roosen, Ber. 1888, 21, 999). M. A. W.

PYRITES, COPPER, *v.* COPPER-PYRITES.

PYRITES (*Ger.* Kies). The ancient name πυρίτης, from πῦρ, fire, was no doubt applied to a variety of minerals that possess, in common with flint, the property of striking fire. In more recent times the name 'pyrites' has been

used for a variety of sulphide minerals possessing a metallic lustre and a fair degree of hardness; and the wide range it covered is well indicated by the title of J. F. Henckel's book, 'Pyritologia, oder Kiess-Historie . . .' (Leipzig, 1725); English translation 'Pyritologia; or, a History of the Pyrites, the principal body in the Mineral Kingdom. In which are considered its names, species, beds, and origin; its iron, copper, unmetallic earth, sulphur, arsenic, silver, gold, original particles, vitriol, and use in smelting' (London, 1757). At the present day the word enters into many compound names, both popular and scientific, of minerals, *e.g.* iron-pyrites or sideropyrite, copper-pyrites or chalcopyrite, arsenical pyrites or arsenopyrite (=mispickel), magnetic pyrites (=pyrrhotite), tin-pyrites (=stannite), cobalt-pyrites (=linnæite), capillary pyrites (=millerite), white pyrites (=mispickel and marcasite), cockscomb- and spear-pyrites (=marcasite), nicopyrite (=pentlandite), argentopyrite, leucopyrite, &c.; whilst in modern German 'Kies' is used still more freely in compound names.

Iron-pyrites (Ger. *Eisenkies*, *Schwefelkies*), in English often called simply 'pyrites,' and by American and French writers 'pyrite.' Iron disulphide (FeS_2) is dimorphous, crystallising either in the cubic or in the orthorhombic system; the former modification is the mineral iron-pyrites and the latter is marcasite (*q.v.*).

Crystals of iron-pyrites are of common occurrence, and they are often beautifully and sharply developed. Their degree of symmetry is that of the pentagonal-dodecahedral (or parallel-faced hemihedral) class of the cubic system. Common forms are the cube, octahedron, and pentagonal-dodecahedron, or combinations of these. The pentagonal-dodecahedron with the indices (210) is, indeed, so characteristic of this mineral that it is known as the pyritohedron. The faces of the cube are each striated parallel to only one pair of edges, and in such a manner that on three adjacent faces the three sets of striations are perpendicular to one another; this, again, is an extremely characteristic feature of crystals of iron-pyrites. Disseminated grains and compact masses are abundant; the mineral also occurs in nodular and stalactitic forms often with an internal radio-fibrous structure. The thermo-electrical properties of iron-pyrites are of interest; some crystals are more strongly thermo-electrically positive than antimony, and others more negative than bismuth, so that the two when placed together give a stronger thermo-electric couple than do antimony and bismuth.

The mineral is opaque with a brass-yellow colour and a bright metallic lustre; its streak is greenish- or brownish-black. There is no distinct cleavage; the mineral is brittle, and breaks with a conchoidal to uneven fracture. The hardness is 6–6½; the mineral scratches glass, and is itself scratched by a knife only with difficulty. These characters enable iron-pyrites to be readily distinguished from other yellow metallic minerals with which it is sometimes confused, *e.g.* copper-pyrites (H.=3½–4, with a deeper yellow colour), and gold (H.=2½–3 and malleable). From marcasite the distinction is less easy in the absence of any distinct crystalline form, for the hardness and colour are nearly the same; marcasite is, however, sometimes rather paler in colour and its sp.gr. (4·8) is a little lower than that of iron-pyrites (4·9–5·1).

When pure, iron-pyrites contains sulphur 53·4, and iron 46·6 p.c. Small quantities of other metals are, however, often present, *e.g.* copper, silver, gold, nickel, cobalt, zinc, tin, thallium, tellurium, selenium, arsenic, &c. But it is probable that these are due to the mechanical admixture of other minerals; for example, in the abundant cupriferous ores of Spain and Norway 1–5 p.c. of copper is present as admixed copper-pyrites. In many gold-mining districts auriferous iron-pyrites is of considerable importance as an ore of gold. The Spanish ores, after roasting for sulphur and extraction of copper from the residues, yield about 1 oz. of gold per 300 tons of ore. The following are analyses of pyritic ore from the more important districts where it is mined: I, Rio Tinto, Huelva, Spain; II, San Domingos, Algarve, Portugal; III, Sain-Bel, dep. Rhône, France; IV, Meggen, Westphalia; V, Röros, Trondhjem, Norway; VI, Chestatee, Dahlonega district, Georgia (E. C. Eckel, Bull. U.S. Geol. Survey, 1903, No. 213, 63).

	I.	II.	III.	IV.	V.[1]	VI.[2]
S	48·50	48·90	46·40	45·60	49·00	43·52
Fe	40·92	43·55	39·00	38·52	42·35	39·70
Cu	4·21	3·10	1·50	—	2·48	3·09
Zn	0·22	0·35	—	6·00	2·01	0·72
Pb	1·52	0·93	—	0·64	0·24	—
As	0·33	0·47	0·10	trace	nil	nil
SiO_2	3·46	0·73	9·25	8·70	1·85	9·26
Al_2O_3	—	—	3·75	—	1·25	2·53
CaO	0·90	0·20	—	—	0·23	—
H_2O	—	0·70	—	—	—	0·36
	100·06	98·93	100·00	99·46	99·63	99·61

[1] Also MgO, 0·22. [2] Also MgO, 0·43.

During the grinding of pyrites for analysis it is found that the material suffers a certain amount of oxidation (*see* E. T. Allen and J. Johnston, The Exact Determination of Sulphur in Pyrite and Marcasite, J. Ind. Eng. Chem. 1910, 2, 196).

Iron-pyrites burns in the air with a small bluish flame, and is capable of supporting its own combustion. This is of importance in the roasting of iron-pyrites for the manufacture of sulphuric acid, and in the 'pyritic smelting' of cupriferous ores. The products of combustion are sulphur dioxide and ferric oxide (the 'purple ore' or 'blue billy' of iron smelters). When heated out of contact with the air, the mineral begins to decompose at about 500°, and finally one-half of the sulphur is expelled. It is insoluble in hydrochloric acid, but decomposed by nitric acid.

Many experiments have been made on iron-pyrites and marcasite with the object of detecting a difference in their chemical constitution, but the results are not concordant. H. N. Stokes (Amer. J. Sci. 1901, 12, 414; Bull. U.S. Geol. Survey, 1901, No. 186, 1–50) has devised a chemical method for discriminating between these minerals and for their quantitative determination in mixtures. This method depends on the fact that when iron-pyrites or marcasite is boiled with an excess of a solution of a ferric salt to complete reduction of the latter, the ratio

of the sulphur oxidised to mineral decomposed is perfectly definite and characteristic of each mineral, provided certain standard and easily controllable conditions are observed. With a boiling solution of ammonium-iron alum containing 1 gr. of ferric iron and 16 c.c. of 25 p.c. free sulphuric acid per litre, the percentage of sulphur oxidised in iron-pyrites is about 60·4, and in marcasite about 18 of the total sulphur. These figures are the characteristic oxidation coefficients, which depend, however, on the temperature and concentration of the solution. The determinations are made in an atmosphere of carbon dioxide, with specially designed apparatus. It is shown, for example, that the nodules, often supposed to be marcasite, so abundant in the chalk-marl at Folkestone, Kent, are really iron-pyrites; one specimen was found to contain iron-pyrites 97 and marcasite 3 p.c. On the artificial production and chemical relationships of pyrites and marcasite, *see* E. T. Allen and others (Amer. J. Sci., 1912, 33, 169).

Iron-pyrites is a mineral of extremely wide distribution. It is found in rocks of all kinds and of all geological ages, either scattered as isolated grains, nodules, and crystals, or collected in veins and large lenticular masses; and the various types of deposits may be of igneous, metamorphic, or sedimentary origin. The best crystallised specimens are from the magnetite mines at Traversella in Piedmont, and the hæmatite mines of Rio in the island of Elba. Good crystals have also been found in the mineral veins of Cornwall and many other mining districts. The deposits of cupriferous iron-pyrites, which are so extensively mined, occur as large lenticular masses in slaty rocks near their contact with igneous rocks. Such deposits are mined at Rio Tinto, Tharsis, Calañas, &c., in the Spanish province of Huelva, and San Domingos in the neighbouring Portuguese province of Algarve; at Sain-Bel, dep. Rhône, France; Rammelsberg in the Harz, and Meggen in Westphalia; Sulitjelma in Arctic Norway, and Röros in southern Norway; Brosso in Piedmont, Italy; Pilley's Island, Newfoundland; Louisa Co. and Prince William Co. in Virginia, and elsewhere in the United States. In the British Isles, pyrites deposits have been worked at the Ovoca mines in Co. Wicklow and at Trefriw in Carnarvonshire. The world's production amounts to about five million tons per annum; of which Spain contributes two-thirds, and Portugal, France, Germany, Norway, and the United States each about a quarter of a million tons per annum.

When subjected to weathering processes near the earth's surface, iron-pyrites is readily decomposed, producing cellular masses of limonite—the so-called gozzans and iron cappings of lodes—which are valuable indications of the presence of metalliferous deposits. At the same time, any gold present in the pyrites is set free, giving a 'free-milling' ore. Two types of the alteration of iron-pyrites may be distinguished. By oxidation in the presence of pure water it gives ferrous sulphate (melanterite), free sulphur, and sulphuric acid; and the latter by its action on the surrounding rocks produces gypsum, various alums, &c. When the oxygenated water contains calcium carbonate in solution the sulphur is removed in the soluble form of gypsum, leaving the iron behind in the form of hydroxide; in this way have been formed the abundant pseudomorphs of limonite and goethite after iron-pyrites.

The principal use of iron-pyrites is for the production of sulphur dioxide in the manufacture of sulphuric acid and in the sulphite wood-pulp process of the paper-maker. It is also used in the preparation of sulphur by simple distillation. The residues after roasting are treated for the extraction of copper, silver, and gold, and finally of iron; to a limited extent they are also used in the making of red paints. By exposing iron-pyrites in heaps to the weather ferrous sulphate (copperas) is prepared in considerable quantities. Pyritous shales, the so-called alum-shales, are utilised in the manufacture of alum. Fragments of crystals have been used in the wave detectors of wireless telegraphy installations. Trivial uses of the mineral are in cheap jewellery, particularly in France and Ireland. It is hard, and takes a fine polish. Polished plates of iron-pyrites, probably used as mirrors, have been found in the graves of the ancient Incas of Peru. In olden times it was used in tinder-boxes and in the wheel-locks of guns.

References.—A. W. G. Wilson, Pyrites in Canada: its Occurrence, Exploitation, Dressing, and Uses (Dept. Mines, Ottawa, 1912, No. 167, 202 pp.); W. C. Phalen (Mineral Resources, U.S. Geol. Survey); H. K. Shearer and J. P. D. Hull, Pyrites Deposits of Georgia (Georgia Geol. Survey, 1918, Bull. 33). L. J. S.

PYROACETIC ACID *v.* ACETIC ACID.

PYROBROMONE. Trade name for bromodimethylamino antipyrine.

PYROCATECHIN, PYROCATECHOL, *v.* PHENOL AND ITS HOMOLOGUES.

PYROCATECHOL-*o*-CARBOXYLIC ACID *v.* PROTOCATECHUIC ACID.

PYROCHLORE. A rare-earth mineral consisting mainly of calcium meta-columbate, but containing also titanium, thorium, zirconium, fluorine, cerium and yttrium metals (5-7 p.c.), sodium, iron, and magnesium. One of the several formula that have been given is $x\mathrm{RNb_2O_6}\cdot y\mathrm{R(Ti,Th)O_3}\cdot z\mathrm{NaF}$. It forms small (up to $\frac{1}{2}$ inch across) cubic octahedra of a dark brown colour with a vitreous to resinous lustre. Sp.gr. 4·2–4·36; H.=5–5½; refractive index high, n_D =2·025; attacked with difficulty by sulphuric acid with evolution of fluorine. It is a mineral of rare occurrence in nepheline-syenites. Localities are: Miass in the southern Urals, Langesund-fjord and Fredriksvärn in southern Norway, Alnö in Sweden, Caucasus, and Madagascar. Crystals of several compounds closely related to pyrochlore have been prepared artificially by P. J. Holmquist (Bull. Geol. Inst. Upsala, 1897, 3, 181). L. J. S.

PYROCOLL *v.* BONE OIL.

PYROCRESOLS $C_{15}H_{14}O$. A group of isomeric bodies, three in number, discovered by Schwarz in coal-tar (Chem. Soc. Abtr. 1883, 204; 1884, 79), and more particularly examined by Bott (J. Soc. Chem. Ind. 1887, 646). They are dimethylxanthenses and are identical with the products obtained by Gladstone and Tribe (Chem. Soc. Trans. 1889, 55, 51) by the de-

composition of the aluminium *o*, *m*, and *p*-tolyloxides.

α-Pyrocresol crystallises in large shining plates, exhibiting a bluish-green fluorescence; readily soluble in benzene, chloroform, carbon tetrachloride, carbon disulphide, &c.; less so in acetic acid, alcohol, or ether; and insoluble in water and alkalis. Soluble also without action in acetyl chloride, phosphorus trichloride, or solution of phosgene gas. M.p. 196°; readily sublimes

β-Pyrocresol. Melts at 124°, and crystallises in small needles or laminæ.

Both the α and β-pyrocresols may be obtained from aluminium *m*-tolyloxide (*cf.* Ruszig, Zeitsch. angew. Chem. 1919, 32, [i.] 37). They have been identified as dimethylxanthenes.

γ-Pyrocresol differs from its isomers by its extreme solubility in all solvents; it invariably crystallises in needles, m.p. 104°–105°, and does not sublime.

These three pyrocresols have also been obtained from the last fraction of the distillate from crude carbolic acid (Zmerzlikar, Monatsh. 1910, 31, 897).

On oxidation with chromic acid in acetic acid solution the pyrocresols yield compounds having the empirical formula $C_{15}H_{12}O_2$.

α-Pyrocresol oxide, m.p. 168°, forms yellowish needles; very soluble in acetic acid and alcohol. According to Zmerzlikar (*l.c.*), this oxide, when fused with potash, yields *m*-cresol, *m*-hydroxytoluic acid and *m*-hydroxyterephthalic acid. It is therefore identical with 4 : 4′-dimethylxanthone and α-pyrocresol is 4 : 4′-dimethylxanthane.

β-Pyrocresol oxide, m.p. 95°.

γ-Pyrocresol oxide, m.p. 77°, crystallises in small rhombic plates, which turn red on exposure to light.

On gentle reduction with hydrogen iodide, the oxides yield pyrocresols, and on very energetic reduction they are decomposed, forming the same reduction products as the pyrocresols themselves, namely, chiefly an oil of formula $C_{15}H_{32}$.

α-Tetranitro-pyrocresol oxide $C_{15}H_8(NO_2)_4O_2$, crystallises from nitrobenzene or glacial acetic acid in small yellowish plates, which, on heating, burn with a flash. Is insoluble in caustic potash, and sparingly soluble in alcohol.

β-Tetranitro-pyrocresol oxide resembles the α- compound, but is more soluble in alcohol.

γ-Tetranitro-pyrocresol oxide forms a granular mass of a pale yellow colour. More soluble in alcohol than the α- compound.

Halogen and sulpho derivatives have also been prepared. *α-Dibromopyrocresol* $C_{15}H_{12}Br_2O$ is obtained in the form of thick, elongated plates; m.p. 215°.

PYRODIN, *Acetylphenylhydrazine, hydracetin,* $C_6H_5{\cdot}N_2H_2{\cdot}C_2H_3O$, was first synthesised by Liebermann. A white crystalline powder, m.p. 128°–130°, very sparingly soluble in cold water and in ether, readily so in hot water, and in alcohol. It possesses very little taste.

Pyrodin is prepared by the interaction of phenylhydrazine with acetic anhydride (Fischer, Annalen, 1877, 190, 129), or with thioacetic acid (Pawlewski, Ber. 1897, 31, 662), and also by other methods (Just, *ibid.* 1886, 19, 1202; Bamberger, *ibid.* 1897, 31, 2630; Leighton, Amer. Chem. J. 20, 677; Baidakowski and] Slepak, J. Russ. Phys. Chem. Soc. 35, 71). It is a powerful antipyretic. It reduces fever temperature quickly, and maintains the temperature at a low level for some hours, producing marked perspiration, but not nausea, vomiting, or collapse. It is especially applicable in cases of pneumonia, scarlet fever, and typhus. Given in small doses in the latter disease it enables the patient to pass through the fever at a low temperature range without delaying the crisis, and it seems also to shorten the period of convalescence. It is less applicable in cases of typhoid, owing to the early exhibition of toxic symptoms. Given in often repeated doses at short intervals it easily shows toxic properties, and these depend on the action on the blood, producing hæmoglobinæmia. It should not be given (unless the temperature be very high) oftener than once in 18 or 24 hours, and it is not safe to continue its use for more than a few days. The dose for children is 2–4 grains, for adults 8–12 grains. It is a much more powerful antipyretic than either antipyrin, antifebrin, or phenacetin; but it is also much more toxic than these bodies. This disadvantage is reduced by the fact that it is rarely necessary to give more than one dose in 12 to 18 hours, as the temperature is kept low for a longer period than by any of the other antipyretics. It reduces the pulse as well as the temperature, and often causes diuresis (J. Dreschfeld, J. Soc. Chem. Ind. 1888, 765; Merck, *ibid.* 1889, 476).

The isomeric acetyl compound

$$C_6H_5N(COCH_3)NH_2$$

has m.p. 125°–126° (Pechmann and Runge, Ber. 1894, 27, 1695; Widman, *ibid.* 2964; Busch and Frey, *ibid.* 1903, 36, 1364).

PYROFULMIN. A yellowish-brown substance obtained by heating mercuric fulminate at 90° for above 100 hours. Is non-explosive, is insoluble in water and neutral to litmus, swells on heating and evolves white choking vapours. Is probably not a definite compound but a mixture of mercuric oxycyanide [$H_9(OCN)CN$] with some mercuric oxide (Langhans, Z. ges. Schiess-u-Sprengstoffw. 1922, 17, 9, 18, 26).

PYROGALLOL (pyrogallic acid, 1 : 2 : 3-trihydroxybenzene) $C_6H_3(OH)_3$ is obtained by the dry distillation of gallic acid (Braconnot, Annalen, 1832, 1, 26; Pelouze, *ibid.* 1834, 10, 159); by fusing hæmatoxylin (Meyer, Ber. 1879, 12, 1392), or α- or β-*p*-chlorophenol sulphonic acid with caustic potash (Peterson and Baehr-Predari, Annalen, 1871, 157, 136, 150). In the form of its methyl ethers it also occurs in beechwood tar creosote (Hofmann, Ber. 1878, 11, 333; Rosauer, Monatsh. 1898, 19, 557).

Preparation.—Gallic acid is heated in a bronze digester with 2 or 3 times its weight of water, at 200°–210°, for about half an hour, in such a manner that the carbon dioxide can readily escape. The resulting pyrogallol solution is heated with animal charcoal, filtered, and rapidly evaporated. The pyrogallol which crystallises out may then be further purified by sublimation or distillation under reduced pressure (Luynes and Esperandieu, Compt. rend. 1865, 61, 487; *see* also D. R. PP. 30648, 32830; Seurbach, Ber. 1877, 10, 38). Gallic acid (10 grms.) may also be heated with glycerol

(30 grms.), at 190°–200°, until carbon dioxide ceases to be evolved (Thorpe, Chem. News. 1881, 43, 109). The yield in both these cases is almost theoretical. Pyrogallol is obtained in nearly theoretical yield by heating solutions or suspensions of tannic or gallic acids at above 160° in an autoclave with a proportion of alkali or alkaline earth hydroxides or carbonates not materially exceeding twice the amount required to effect substitution of the hydrogen atoms of the carboxyl groups initially present, and those formed by hydrolysis, if any (Nitritfabrik Akt. Ges., Eng. Pat. 140694). Pyragallol may also be prepared by heating gallic acid with 2 parts of coarsely powdered sulphur (Liebig, Annalen, 1857, 101, 48), or with twice its weight of aniline at 120°; the *aniline pyrogallate*, m.p. 55°–56°, so obtained is treated with benzene or toluene, when pure pyrogallol is precipitated (Cazeneuve, Compt. rend. 1892, 114, 1485), or by heating pyrogallol-4-sulphonic acid with dilute mineral acids in a sealed tube for 8 hours at 200° (D. R. P. 207374; Frdl. 1907–10, 143).

Properties.—Pyrogallol forms white lustrous laminæ or fine needles, m.p. 132·5°–133·5°, b.p. 292°–294° at 730 mm. (decomp.). It is odourless, has a bitter taste, and is poisonous. It is readily soluble in alcohol, ether, and in water, dissolving in $2\frac{1}{2}$ parts of water at 13°. When exposed to air its aqueous solution turns brown rapidly, but its alcoholic solution turns brown more rapidly when kept in a stoppered bottle; both solutions may, however, be preserved indefinitely by the addition of a small quantity of sodium bisulphite (Lumière and Seyewetz, J. Soc. Chem. Ind. 1908, 183). The alkaline solution also turns brown on exposure to air owing to the absorption of oxygen, and this property is made use of in the estimation of oxygen; unless, however, a sufficient excess of alkali is present, much carbon monoxide is evolved (Clowes, Chem. Soc. Proc. 1895, 200; *see* also Liebig, Annalen, 1851, 77, 107; Weyland and Zeitler, *ibid.* 1880, 205, 264; Weyl and Goth, Ber. 1881, 14, 2666; Calvert, Compt. rend. 1863, 57, 873 Cloëz, *ibid.* 875; Boussingault, *ibid.* 886; Berthelot, *ibid.* 1898, 126, 1459; also art. Analysis). The oxidation of pyrogallol in potassium hydroxide solution gives, among other products, 2 : 3 : 2′ : 3′ : 2″ : 3″-*hexahydroxytriphenoquinone* (Nierenstein, Chem. Soc. Trans. 1915, 1217). When a solution of pyrogallol is mixed with hydrogen peroxide in presence of certain colloidal metal and metallic oxide sols. oxidation occurs rapidly with the production of white light, even in presence of colloidal platinum of concentrations as low as 1 part in 250,000 (Goss, J. Biol. Chem. 1917, 31, 271). Similar effects are produced by chromates, dichromates, hypochlorites, iron salts, silver, and silver oxide and other substances. For conditions determining the intensity of the light, *see* Harvey (J. Biol. Chem. 1917, 31, 311).

Under the influence of the silent electric discharge small quantities of hydrogen and carbon monoxide are evolved.

When hydrogenated in the presence of finely divided nickel, cyclo-hexane-1 : 2 : 3-triol, m.p. 67°, is formed (Sabatier and Mailhe, Compt. rend. 1908, 146, 1196).

When dissolved in baryta water and shaken with air, it forms hexahydroxydiphenyl (Harries, Ber. 1902, 35, 2954), whilst when oxidised electrolytically it yields purpurogallin (Perkin, Chem. Soc. Trans. 1904, 244). The latter is also obtained together with a substance $C_{12}H_{10}O_7$ when an alcoholic solution of pyrogallol is treated with acetic acid, then with *iso*amyl nitrite, and the product boiled with water (Perkin and Steven, *ibid.* 1906, 802).

Pyrogallol rapidly reduces gold, silver, and mercury salts even in the cold. Pure ferrous salts, when added to aqueous pyrogallol, give a white turbidity, which becomes blue on addition of sodium hydroxide or in the presence of a trace of ferric salt. In the absence of alkali the blue colour rapidly changes to red-brown, this change also being induced by the addition of mineral acids. Organic iron salts also give a blue coloration (Hirsch, Chem. Zentr. 1899, i. 927). When agitated with potassium cyanide pyrogallol gives a yellow-red coloration, which turns to yellow-brown on addition of hydrogen peroxide (Griggi, Chem. Zentr. 1899, i. 454). In this way it can be distinguished from gallic acid, which gives a ruby-red colour with the first reagent, and from digallic acid, which gives a dirty white with the second.

Five mgrms. of pyrogallol dropped on to a melted mixture of 45 of ammonium nitrate, 34 of lead nitrate, and 21 of lead oxide produces a chrome-green colour (Mathieu-Plessy, Bull. Soc. Ind. Mulhouse, 1890, 69).

When treated with strong sulphuric acid and alcoholic tartaric acid, pyrogallol yields a liquid which first exhibits violet striæ, and then assumes a uniform intense violet colour. On dilution with water the violet colour disappears. If lactic acid is used instead of tartaric, an orange-red colour is obtained, which does not disappear on dilution (Carletti, Boll. Chim. Farm. 1909, 48, 441).

With formalin and sulphuric acid, pyrogallol gives a red colour (Endemann, J. Soc. Chem. Ind. 1896, 791); in the presence of ammonia water a product, used in the treatment of bad smelling wounds, ulcers, &c., is formed (D. R. P. 99570; Frdl. 1907–1910, 724). When heated with aldehyde and sulphuric acid, it forms a crystalline compound $C_8H_8O_3,2H_2O$ (Causse, Bull. Soc. Chim. [iii.] 3, 861).

When pyrogallol is heated with benzaldehyde in the presence of zinc chloride or of fuming sulphuric acid, red substances, having the properties of aurine dyes, are formed (Hofmann, Ber. 1893, 26, 1139).

An aqueous solution of pyrogallol is turned brown by nitrous acid, and is oxidised by nitric acid to carbon dioxide and oxalic acid (Rösing, J. 1857, 315; Jacquemin, Bull. Soc. Chim. 1873, 21, 435; *see* also Oppenheimer, Ber. 1903, 36, 1744).

Derivatives.—Pyrogallol monosulphonic acid $C_6H_2(OH)_3HSO_3$ is obtained by treating pyrogallol with sulphuric acid of sp.gr. 1·84 at about 100° (Delage, Compt. rend. 1900, 131, 450; Schiff, Annalen, 1875, 178, 171; *see* also D. R. P. 207374; Frdl. 1907–10, 143); by treating the product with fuming sulphuric acid, the *disulphonic acid* is obtained (Delage, *ibid.* 1901, 132, 421). The mono- acid acts as a dibasic acid, whilst the disulphonic acid acts as a tribasic acid, this being due to the fact that one of the

hydroxyl groups in pyrogallol is acidic (Delage, *ibid.* 1901, 133, 297).

When solutions of the hydroxide of calcium, barium, or strontium are added to the corresponding pyrogallol mono-, or di-sulphonate, coloured substances are produced, the composition of which varies with the conditions of the experiment. Six such compounds have been obtained, varying in colour from violet to blue. They are soluble in acids, giving yellow solutions, and their solubility in water and in alcohol increases with increasing molecular weight of the base and the number of sulphonic groups. They oxidise rapidly in the moist state, but when dry are fairly stable. When deposited on silk they turn green, then yellow (Delage, Compt. rend. 1903, 136, 893, 1202; also *ibid.* 760 and *l.c.*).

Pyrogallol sulphonic acid has been employed in dyeing hair (D. R. P. 185041; Frdl. 1907–10, 851). The sulphonic acids also combine with nitroso aromatic and aryl amines, forming gallocyanine sulphonic acids, which give blue to violet shades on wool (D. R. PP. 203145, 214063; Frdl. 1907–10, 247, 253).

For amino and nitro derivatives, *see* Schiffer, Ber. 1892, 25, 721.

Pyrogallol carboxylic acid. *See* Gallic acid.

Pyrogallol carbothioxylic acid

$$C_6H_2(OH)_3CS_2H,H_2O$$

forms beautiful glistening golden scales which become anhydrous at 70° and have m.p. 154° (Lippmann, Monatsh. 1889, 10, 617).

Pyrogallol monomethyl ether $C_6H_3(OH)_2OMe$ is obtained by fusing guaiacol sulphonic acid with sodium hydroxide. It has m.p. 66°–67°, and dissolves in aqueous alkali with a green colour, which gradually turns brown. It reduces silver nitrate, especially on warming (D. R. P. 109789).

Pyrogallol dimethyl ether $C_6H_3(OMe)_2OH$ can be isolated from beechwood tar creosote by treating the fraction boiling at 250°–270° with benzoyl chloride and decomposing the product with alkali (Hofmann, Ber. 1878, 11, 1455; *ibid.* 1879, 12, 1377, 2216; Rosauer, Monatsh. 1898, 19, 557; D. R. P. 9328).

Pyrogallol dimethyl ether is obtained pure by heating syringic acid at 240°–270°. It forms crystals, m.p. 54·8°, b.p. 262·7° (*see* also D. R. P. 162658, and Rosauer, *l.c.*). It yields a *picrate*, m.p. 61°, and an *acetyl* derivative, m.p. 53·5°, and when oxidised with sodium nitrite in acid solution, or by other oxidising agents, it is converted into *cedriret* (Graebe and Hess, Annalen, 1905, 340, 232). When mixed with the dimethyl ether of methyl pyrogallol and caustic soda and oxidised by heating in air at 200°, it yields pittacal or eupittonic acid, which dyes silk orange in an acid bath, but is of little value as a dye (Hofmann, *l.c.*). Colouring matters are also obtained when the pyrogallol ethers are treated with chloroform, carbon tetrachloride, or hexachlorethane in the presence of alkalis. When the dimethyl ether is treated with tiglic aldehyde, a resin, $C_{21}H_{26}O_6$, is obtained (Doebner, Arch. Pharm. 1896, 234, 610).

Freshly prepared pyrogallol dimethyl ether can be employed as a delicate reagent for the detection of chromic acid, ferric salts, nitrous acid, and other oxidising agents, with which it gives a red or yellow coloration (Meyerfeld, Chem. Zeit. 1910, 34, 948).

The *trimethyl ether* (Will, Ber. 1888, 21, 607; Perkin, Chem. Soc. Trans. 1896, 1241; Boyd and Pitman, *ibid.* 1905, 1255) and the *ethyl ethers* (Hofmann, Ber. 1878, 11, 798; Hirschel, Monatsh. 1902, 23, 181; D. R. P. 162658). For other alkyl ethers, *see* Herzig and Pollack (Monatsh. 1902, 23, 700; *ibid.* 1904, 21, 505 and 808; Ber. 1903, 36, 660); Bogert and Plaut (J. Amer. Chem. Soc. 1915, 37, 2723); Krauss and Crede (*ibid.* 1917, 39, 1431); Bogert and Ehrlich (*ibid.* 1919, 41, 798).

The *carbamic esters* of pyrogallol-1 : 3-dialkyl ethers are prepared by treating the ethers with carbamic chloride ($ClCONH_2$) in ethereal solution or by the interaction of phosgene with a salt of pyrogallol dialkyl ether and then converting the chloroformic acid ester of the pyrogallol ether so formed into the carbamic acid ester by the action of ammonia (D. R. P. 194034; Frdl. 1907–10, 917).

Pyrogallol and its alkyl ethers combine with chloracetic acid on boiling with sodium hydroxide in a reflux apparatus. The condensation product separates on acidifying with hydrochloric acid, and may be recrystallised from water (D. R. P. 155568; Frdl. 1902–1904, 102).

Pyrogallol glycollic acid, m.p. 153°–154°, *pyrogallol diglycollic acid*, *pyrogallol ethyl ether diglycollic acid*, m.p. 108°–109°, and *pyrogallol diethyl ether glycollic acid*, m.p. 82°–83°, have been prepared. Unlike pyrogallol, these derivatives are not poisonous, and can be used in the treatment of skin diseases. They are also said to be useful in photography and in the manufacture of dyestuffs.

Pyrogallol (20 parts) reacts with succinic anhydride (10 parts) at 150°–170°, using zinc chloride as condensing agent; it yields amongst other dyestuffs, pyrogallol succineïn, an analogue of galeïn and digallacyl, which gives yellow colours with alumina and grey with iron mordants (Georgievics, Monatsh. 1899, 20, 450).

Pyrogallol succineïn $C_{16}H_{14}O_8$, purified by means of its sulphuric acid compound, forms a red powder, almost insoluble in ordinary solvents, and decomposes at 180°. It combines with 1 molecule of hydrochloric acid to form brownish plates.

Digallacyl, $C_{16}H_{14}O_8$, crystallises from alcohol in needles or plates, and turns dark at 270° without melting. It dissolves in soda lye, forming a yellow solution, which on oxidation turns greenish and deposits a yellow flocculent precipitate. Digallacyl dissolves in strong sulphuric acid with a yellow colour, and on heating or adding ferric chloride the solution turns an intense violet colour. On careful dilution, a greenish precipitate is formed, which on filtration and treatment with sulphuric acid again gives a violet solution.

Pyrogallol benzeïn, $C_{38}H_{24}O_{11}$, is obtained by heating benzotrichloride with pyrogallol. The chloride so formed is decomposed by boiling it with water, and the benzeïn is recrystallised from glacial acetic acid. Its dyeing properties are of little importance. A number of its derivatives have been prepared (Doebner and Foerster, Annalen, 1890, 257, 60). *Hydropyrogallol benzeïn* $C_{19}H_{14}O_5,3H_2O$, formed by

the reduction of the above compound, forms reddish needles. A dyestuff is also obtained by the action of acet-*p*-toluidine on pyrogallol in the presence of phosphorus oxychloride (D. R. P. 140421; Frdl. 1902–1904, 349), and violet to blue dyestuffs are formed by the interaction of pyrogallol with a number of *p*-dialkylamino-*o*-hydroxybenzobenzoic acids in the presence of sulphuric acid (D. R. P. 122359; Frdl. 1900–1902, 280).

Pyrogallol forms condensation products with acetone and with methyl ethyl ketone (Fabinezi and Szeki, Ber. 1905, 38, 3527).

Pyrogallol forms additive products with aliphalic amines, and some of these are used in photography. *Dimethylamine pyrogallol* $C_6H_3(OH)_3 \cdot NHMe_2$ crystallises in prisms, m.p. 163°, dissolves readily in water, is sparingly soluble in alcohol, and insoluble in ether. *Trimethylamine pyrogallol* melts at 160° (D. R. P. 141101; Frdl. 1900–1902, 1218).

Pyrogallol also combines with gallocyanine (D. R. P. 77452; Frdl. 1894–1897, 496), with a number of diazo compounds (D. R. PP. 81109, 81376, 8266; Frdl. 1890–1894, 637, 648; *ibid.* 1894–1897, 797, 798), and with other compounds forming useful dyes (D. R. PP. 4914, 50450; 50451, 54661, 72446, 58483, 59863, 61326; Frdl. 1890–1894, 120, 147, 150, 272; 1887–1890, 481–485).

Monoacetyl pyrogallol (*Eugallol*)

$$C_6H_3(OH)_2O \cdot COCH_3$$

is obtained by heating the tri- or the di- acetate with pyrogallol to about 160°. It distils at 185°/25 mm. (D. R. PP. 104663, 122145; Frdl. 1900–1902, 1119).

Diacetyl pyrogallol has m.p. 110°–111° (D. R. P. 104663).

Triacetyl pyrogallol (*lenigallol*), obtained by heating pyrogallol (200 parts) with acetic anhydride (500 parts) and 1 part of strong sulphuric acid, is a white crystalline powder, m.p. 165° (D. R. P. 124408; Frdl. 1900–1902, 1119; Perkin and Simonsen, Chem. Soc. Trans. 1905, 858). The acetyl compounds are employed in medicine.

Pyrogallol (2 mols.) reacts with vanillin (1 mol.), forming *pyrogallol vanillein* $C_{20}H_{18}O_8$, colourless crystals which turn intensely blue with a minute trace of hydrochloric acid (Etti, Monatsh. 1882, 8, 677).

Caffeine-pyragallol

$$C_8H_{10}O_2N_4,C_6H_6O_3,4H_2O$$

is formed by mixing equivalent quantities of the constituents in warm aqueous solutions. It consists of needle-shaped crystals, m.p. 70° (Ultée, Chem. Zentr. 1910, i. 519).

Pyrogallol aldoxime forms white lustrous plates, m.p. 203°–204° (D. R. P. 114195; Frdl. 1900–1902, 121).

Alloxan pyrogallol needles or prisms, which decompose at 230° (D. R. PP. 107720, 113722; Frdl. 1900–1902, 163).

Pyrogallol carbonate $HO \cdot C_6H_3 \langle \begin{matrix} O \\ O \end{matrix} \rangle CO$, colourless needles, m.p. 132°–123°, is formed by passing phosgene gas into a solution of pyrogallol in a mixture of pyridine and xylene. If more phosgene is employed, *dipyrogallol tricarbonate* $CO(O \cdot C_6H_3 \langle \begin{matrix} O \\ O \end{matrix} \rangle CO)_2$, colourless leaflets, m.p. 177°, is formed (Einhorn, Cobliner, and Pfeifer, Ber. 1904, 37, 100). The benzoyl, methyl, bromo, nitro, and other derivatives of the carbonate are described by these authors. Fuming nitric and sulphuric acids convert the carbonate into 4 : 6-*dinitropyrogallol*

$$C_6H(NO_2)_2(OH)_3$$

m.p. 208°. It also combines with quinoline triethylamine, and other substances.

Pyrogallol piperidine $C_5H_{11}N,C_6H_6O_3$, forms white needles which evolve gas at 110°, become discoloured at 140°, and melt at 171° (Rosenheim and Schidrowitz, Chem. Soc. Trans. 1898, 142).

Pyrogallol-antipyrin $C_6H_3(OH)_3,C_{11}H_{12}N_2O$ separates as an oil on mixing concentrated solutions of pyrogallol and antipyrin. It forms colourless crystals, m.p. 77°–78° (Patein and Dufau, Bull. Soc. chim. 1897, [iii.] 15. 1048).

Pyrogallol quinoline. *See* PURPUROGALLIN.

Pyrogallol glycoisoquinoline forms small rose-coloured hexagonal plates and yields a *hydrochloride* and a *platinochloride.*

Pyrogallolglycotetrahydroquinoline

$$C_6H_2(OH)_3CO \cdot CH_2 \cdot C_9NH_{10}$$

forms yellow crystals, m.p. 177°–178°. It yields amorphous yellow metallic salts, does not combine with acids, and gives a crystalline *sulphonic acid* derivative, m.p. 188°. With phenylhydrazine, it forms the compound $C_6H_2(OH)_3C(N \cdot NHPh)CH_2 \cdot NH \cdot NHPh$, which crystallises in slender, yellow, silky needles, m.p. 214°–215° (Nencki, Ber. 1894, 27, 1969).

Pyrogallol also combines with naphthoquinone, yielding products which are employed in pharmaceutical and dyestuff preparations (D. R. P. 96565; Frdl. 1897–1900, 671).

For *halogen* derivatives of pyragallol, *see* Will (*l.c.*), Peratonner (Gazz. chim. ital. 28, i. 227), Biétrix (Compt. rend. 1896, 122, 1545), Perkin and Simonsen (*l.c.*).

For the metallic derivatives, *see* Causse and Bayard (Compt. rend. 1892, 115, 507), De Forcrand (*ibid.* 46), Causse (*ibid.* 1893 117, 232), Godeffroy (Chem. Zentr. 1895, ii. 159), Kunz and Krause (Arch. Pharm. 1898, 236, 542); Weinland and Denzel (Ber. 1914, 47, 2753). A number of other derivatives of pyrogallol have been described (Dzierzgowski, Ber. 1894, 27, 1988; Bistrzycki and Oehlert, *ibid.* 2632; Syniewski, *ibid.* 1895, 28, 1874; Dimroth and Zoeppritz, *ibid.* 1902, 35, 993; Godeffroy, J. Soc. Chem. Ind. 1895, 650; Bartolotti, Gazz. chim. ital. 1896, 26, ii. 433; *ibid.* 1897, 27, i. 289; Rosauer, *l.c.*; Graebe and Suter, Annalen, 1905, 340, 222; Gattermann, *ibid.* 1907, 357, 313; Perkin and Weizmann, Chem. Soc. Trans. 1906, 1649); Ghiglieno, Atti R. Accad. Sci. Torino, 1913, 47, 16; Heller and Fritsch, Ber. 1912, 45, 2389; Voswinckel and De Weerth, Ber. 1912, 45, 1242; Dutta and Watson, Chem. Soc. Trans. 1912, 1241; Schestakov and Nocken, Ber. 1914, 47, 331.) *V.* also PHENOL AND ITS HOMOLOGUES.

For the use of pyrogallol in photography, *v.* art. PHOTOGRAPHY.

PYROGUAIACIN *v. Guaiacum*, art. RESINS.

PYROLIGNATES, PYROLIGNEOUS ACID, *v.* ACETIC ACID.

PYROLUSITE. An important ore of manganese, consisting essentially of manganese

dioxide (MnO_2); but being amorphous and a final product of the decomposition of other manganese minerals, it is frequently more or less impure. It forms earthy to granular masses with an iron-black to steel-grey colour and submetallic lustre; the streak is bluish-black, and the mineral is soft enough (H.=2) to soil the fingers. Sometimes it shows a fibrous or columnar structure (sp.gr. 4·88), or crystals more or less distinct in form (sp.gr. 4·75). These are, however, pseudomorphous forms, and are due to the alteration of crystallised manganite to pyrolusite. Manganese dioxide crystallises in the tetragonal system, and is represented by the rare mineral polianite. Pyrolusite occurs, together with psilomelane (*q.v.*) and other black manganese oxides, usually as beds and pockets in clay overlying limestones, or as a weathering product of crystalline rocks rich in manganese silicates. The known localities are numerous. The ore is mined at the Lindener Mark near Giessen, Ilmenau in Thuringia, Vorderehrensdorf in Moravia, Platten in Bohemia, Carnarvonshire and Merionethshire in North Wales; and more extensively in the Caucasus and elsewhere in southern Russia, Greece, Brazil, United States, India, &c.

The name pyrolusite (from πῦρ, fire, and λύειν, to wash) has reference to the well-known use of the mineral in decolorising glass. Other applications in which the mineral acts as an oxidising agent are in the preparation of chlorine, bromine, and oxygen; in electric batteries; as a dryer in varnishes and paints; and in the manufacture of manganates and permanganates used as disinfectants. As a colouring material, it is used in the manufacture of green and violet paints; in the colouring of glass, pottery and pottery glazes, and bricks; and in dyeing and calico-printing. The principal use, however, of the mineral at the present day is in the manufacture of iron and steel; the ore being used either directly in the smelting or at some later stage in the form of ferromanganese or spiegeleisen. It is also used for the manufacture of manganese-bronze and some other alloys.

References.—Manganese, 1913–1919 (Imp. Min. Res. Bur. London, 1921). On the manganese ore deposits of India, L. L. Fermor (Mem. Geol. Survey, India, 1909, 37). In England, Wales, and Scotland, *v.* Special Reports on the Mineral Resources of Great Britain (Mem. Geol. Survey, 2nd ed. 1916, i). In U.S.A., E. C. Harder, Manganese Deposits of the United States, with sections on Foreign Deposits, Chemistry and Uses (with bibliography) (Bull. U.S. Geol. Survey, 1910, No. 427); H. Ries, Economic Geology, New York, 1916. L. J. S.

PYROMETRY. The first attempt to record temperatures for industrial purposes may be said to have been made by Josiah Wedgwood in 1782. The instrument he devised depended on the permanent contraction of fire-clay when subjected to a high temperature, and remained the standard for nearly a century. In 1882 the famous Sèvres pottery employed fusible clay to determine the temperature necessary for their work. This method was perfected in 1886 by Seger, who constructed cones of clay of varying composition with fusing points ranging from 600° to 1800°. The substances which enter into the composition of these cones are essentially pure quartz sand, Norwegian felspar, carbonate of lime, Zettlitz kaolin, consisting of silica, alumina, oxide of iron and water. In very fusible cones oxide of iron, oxide of lead, carbonate of soda and boric acid are added. The less fusible cones contain calcined alumina. These cones are extensively used to-day, chiefly on account of their simplicity and cheapness. The cones are in the form of triangular pyramids about 15 mm. on a side and 50 mm. high. Under the action of heat they finally soften and bend. The desired temperature is reached when the apex has bent halfway over and points downwards. A further increase of temperature causes the cone to melt completely. The fusing-points of the various mixtures have been carefully determined at the Berlin porcelain works by comparison with an accurate pyrometer. The cones are supplied by number, the less fusible for high temperatures extend from 1 to 38, the highest being about 1980°. The more fusible are numbered from 01 to 022, the lowest temperature being at 590°. The cones 28 to 38 are derived from cone 27 by the addition of increasing quantities of Al_2O_3. The cones 5 to 28 from the cone 5 by the addition of increasing quantities of the mixture $Al_2O_3+10SiO_2$. Cones 1 to 5 from cone 1 by replacing increasing quantities of sesquioxide of iron by alumina. For the other series of cones Nos. 010 to 1 are obtained from cone 1 by the substitution of boric acid for silica. Cones 022 to 011 are derived from cone 022 by the addition of increasing quantities of the mixture

$$Al_2O_3+2SiO_2$$

While these cones are useful for the attainment of any particular temperature in a furnace, they can be no guide in maintaining a steady temperature, and can be successfully used only in such cases where a furnace is carried to the desired point and then allowed to cool off. In the ceramic industry they are generally used, and before firing a series of cones is introduced so that the attainment of successive temperatures may be observed by the falling over of the tips of the various cones in order of fusibility. As general temperature indicators, they are undoubtedly useful, and even in cases where more expensive means are adopted to measure the temperature of a furnace. Other forms of fusion pyrometers have been devised from time to time. Coils of wire of the various metals have been used, such as the Prinsep alloys (range 620°–1225°) (Ann. Chim. 1829, 41, 247); but these are less easily observed, and give by no means so fine a method of indicating temperatures as the Seger cones.

Brearley and Moorwood's sentinel pyrometers (Jour. Iron and Steel Inst. 1907, 68, 261) have been prepared for steel-hardening furnaces. These depend on the precise character of the metling-point of pure sodium or potassium chlorides. These salts are cast into cylinders and placed in small porcelain saucers upon the floor of the furnace or oven to be controlled. When the temperature rises, the potassium chloride cylinder remains erect, and retains its form absolutely until 735°–736° is exceeded and 740° is reached, when it melts down to a clear liquid. In the same way sodium chloride and barium chloride melt in their turn. In order

to cover the range from 630° to 770°, various combinations of sodium chloride and potassium chloride have been made. The gradual addition of potassium chloride, or *vice versâ*, lowers the melting-point until with 1 molecule of each salt the lowest attainable point is reached. Other ranges of temperature may be observed among different salts. Thus mixtures of sodium and potassium sulphates give a range from about 800°–1050°. The indications of the sentinels are sharper than the Seger cones, which gradually soften at first and often leave some doubt as to the exact temperature attained.

The observation of the boiling-point of liquid alloys of sodium and potassium has been suggested by Baly and Chorley. This may be used up to 600°, but cannot be said to be a form of measurement suitable for industrial purposes.

General Expansion Methods.

The measurement of temperature by the expansion of various materials forms the basis of a large number of instruments. With the exception of the ordinary air or hydrogen thermometer, all the commercial instruments are empirical in character. It is hardly within the scope of this article to deal with the standard gas thermometer. It should be understood, however, that all the temperature indications of the commercial instruments should be expressed in terms of the normal hydrogen scale. While local conditions may be adequately met by individual scales easily reproduced, these are but makeshifts, and should be replaced by standard instruments or by reference to a standard pyrometer.

The well-known mercury-in-glass thermometer is adapted for ranges higher than the boiling-point of mercury by the use of hard glass or quartz and the introduction of nitrogen under pressure into the tube. Commercial instruments are available reading to 500°C. or 600°C., but the pressure is so high (30 atmospheres or more) that they are exceedingly liable to break.

The use of bars of metal has been in vogue for a very long time, and many different forms of instruments have been devised. One often met with at the present time is that of Schäffer and Budenberg. It consists of an outer tube of iron surrounding a rod of copper attached at the end. The tubes are usually 2 ft. 6 ins. long, attached to a dial gauge for showing the relative expansion of the two metals. The relative movement of the metals is magnified by a system of levers. The range of the instrument is from 212°F. to 720°F. Some other forms such as those of Daniell, Steinle and Harting employ bars of metal inclosed in earthenware and graphite respectively, and may be used for much higher temperatures.

Various practical air pyrometers have been proposed. The pyrometer of Heisch and Folkard is a simplified air thermometer reading only to 500°C. The form of air pyrometer devised by Wiborgh (Trans. A. I. Min. E. 1892; also Jour. Iron and Steel Inst. 1882, 2, 110) consists of a porcelain bulb containing air at suitable initial pressure. The bulb is attached to a metal tube communicating with a collapsible vessel operating a registering device similar to a Bourdon steam gauge. The increase in air pressure due to rise of temperature is effective in operating the gauge, on which a scale of temperature is placed, ranging from ordinary temperature up to 2400°F. The instrument is similar in appearance to the metal expansion thermometer, and, like it, is subject to errors due to the magnifying device for producing a large open scale. It is, however, more fragile owing to the porcelain bulb, and the scale has to be set frequently when the pyrometer is cool.

The Bristol air pyrometer is well known in America, and has the advantage of combining a recording gauge. The bulb is metallic, and is attached to many feet of flexible metallic tubing. It is not used, however, for temperatures over 500°F. or 600°F.

The expansive power of the vapour of many liquids above their normal boiling-points has been highly recommended as a suitable means for measuring high temperatures. Thus Schäffer and Budenberg's thalpotassimeter is a type of instrument employing this method. It is similar in appearance to their metal expansion thermometer, but the increase in pressure of the vapour is used as in Wiborgh's air thermometer to operate a pressure gauge. For temperatures of 92°F. to 250°F., ether is employed as the source of vapour, from 212°F. to 650°F. water is used, and from 650°F. to 1400°F. mercury is the working substance. Whilst it may be said that the first two are serviceable, it cannot be said that the last one is durable enough for practical purposes, on account of the destructive action of the mercury vapour on the metal parts.

Transpiration pyrometers.—A pyrometer has been devised by Frews which in principle is a continuous air thermometer. The pressure of air flowing out of a fine opening in a tube is adjusted when cold. When the tube is heated the back pressure, which results from the volume increase, is recorded, and gives a measure of the temperature.

The best known transpiration pyrometer is that of Uehling and Steinbart (Stahl u. Eisen, 1899, 19, 431; Jour. Iron and Steel Inst. 1904, 65, 124) (*see* Fig. 1). Air, carefully filtered, is

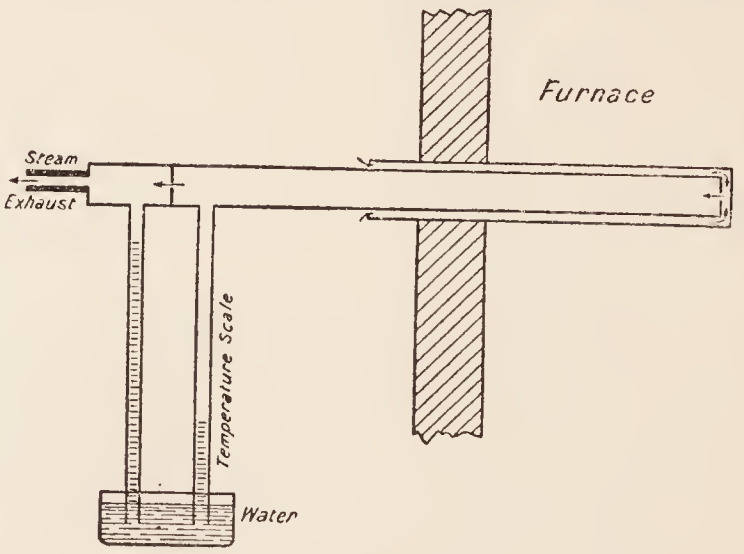


Fig. 1.

drawn through a fine opening in the end of a fine platinum tube surrounded by a second platinum tube exposed to the heat of the furnace. This air is sucked through a second

fine tube after being cooled down to a temperature of 212°F. A steam-blast exhaust serves to maintain a constant suction. It is obvious that owing to the suction of the air a difference in pressure will result between the two sides of the second fine tube. Owing to the expansion of the air passing through the first heated tube, this difference in pressure decreases with rising temperature, and a suitable manometer tube may be used as an indicator of the temperature of the heated air. The rising and falling column of water in the manometer tube indicates on a scale a rising and falling temperature. The pyrometer can readily be made self-recording by attaching a float over the liquid in the manometer tube. To the float is attached gear which operates a pen moving over a rotating drum. The instrument has extensive use in blast-furnace work, in spite of its high cost. This is chiefly due to the permanent character of the installation. The pyrometer is not portable, and hence there is less liability of breakage in transferring it from one furnace to another.

A transpiration pyrometer, known as the Krupp's pyrometer (von Bergen, Jour. Iron and Steel Inst. 1886, 1, 207, also known as the Hobson hot-blast pyrometer), has been devised by which ordinary mercury thermometers can be used to measure the temperature of the hot blast. Cool air in suitable proportions is mixed with a stream of the hot gases drawn out through a side tube in the hot-blast main. It is based on the assumption that the ratio of the amount of hot gas to cold air is the same, whatever the pressure of the hot blast.

Specific heat pyrometer.—While at one time most of the best pyrometric methods were based on the measurement of the heat absorbed by a known mass of metal immersed in a furnace, at the present time there appears to be little reason for their continuation.

The water pyrometer of Siemens is based on this principle, and was formerly widely used for industrial purposes. It seems hardly necessary to do more than mention it here, since it has been practically superseded by more modern and more convenient methods.

The conducting of heat out of a furnace by a metal rod such as Jourde's method has been used to indicate the temperature of the furnace. This method cannot, however, be said to be of industrial application.

Wiborgh's thermophone pyrometer consists of small calcined cylinders which are placed in the furnace and explode with a sharp crack at the end of an interval of time corresponding to the temperature of the furnace. Their range is from 600°F. to 4000°F. In practice they are placed in the furnace, and the time up to the moment of explosion gives a means of calculating from a table the temperature.

Electrical pyrometry.—Electrical pyrometers may be divided into two classes, those making use of the thermoelectric properties of the metals first discovered by Seebeck in 1820 and applied by Becquerel in 1830, and those in which the change in resistance of a metal wire with temperature is employed. It is to the researches of C. Barus (Bull. U.S. Geol. Survey, 1889, 54; Phil. Mag. 1892, [v.] 34, 1) and Le Chatelier (Bull. Soc. Chem. 1887, 47, 2, 300) that we owe our knowledge of the most serviceable high-temperature thermoelectric pyrometer. Barus experimented with wires of platinum and an alloy of platinum and 10 p.c. iridium. He found that the junction of the pure metal and the alloy formed a thermocouple of great reliability over the range 300°–1500°C. Le Chatelier studied a junction of platinum with an alloy of platinum and 10 p.c. rhodium. Subsequent researches by A. L. Day and by Holborn and Day (Wied. Ann. 1899, 68, 817; Drude's Ann. 1901, 4, 99) have shown that the rhodium alloy stands the high temperature better. From the thermoelectric table of the metals pairs of metals may be selected giving large electromotive forces, but exhaustive research has found none to equal the couple of Le Chatelier in standing the destructive action of even a moderately high temperature for any length of time.

They are all based on the same general principle. One end, the hot junction, is composed of the two metals fused or soldered together, and the other end consists of the cold junction, where the wires, having passed out of the furnace, are maintained at a uniform temperature either at a 0°C. or at the temperature of the room. From the 'cold end,' wires pass to a galvanometer or millivoltmeter, and the temperature may be indicated directly on the scale. The modern development of the portable galvanometer has very much facilitated the use of the thermojunction. The correctness of reading depends as much on the cold end as on the hot end, and hence great care must be exercised to have the wires of the couple sufficiently long to be away from the influence of the furnace. This is an expensive matter with the platinum thermocouple, but the use of a water-cooled 'cold end' helps to correct this disadvantage. The E.M.F. developed in microvolts for the platinum-rhodium and platinum-iridium thermocouple is given in the following table :—

Temp.	Ir.	Rh.
100°C.	517	565
448°C.	3228	3450
930°C.	11000	8500
1500°C.		15100

The expression found to hold for the Reichsanstalt standard junction which is usually supplied is given in microvolts as follows, to hold only between 300°F. and 1100°F.

$$E = -310 + 8{\cdot}048t + 0{\cdot}00172t^2$$

when the cold junction is maintained in melting ice.

In obtaining temperatures by one of these couples it is much more practical to determine accurately a number of fixed points, measuring at the same time the E.M.F. developed between the hot junction and the cold junction in ice. A suitable potentiometer for such work may be readily made or obtained from any of the standard instrument companies. The following gives the melting-points of a number of convenient metals :—

Metal	Melting-point
Zinc	419·0
Aluminium	657·0
Silver	961·5
Copper	1065·0

A curve showing the relation between E.M.F.

developed and temperature can be readily obtained, and becomes a calibration curve from which any temperature within the range can be determined.

For industrial purposes there are portable galvanometers available, such as the galvanometer of Le Chatelier, which are calibrated, directly in degrees. The thermojunction itself is protected in a porcelain tube from the direct action of the furnace gases. This is very necessary, inasmuch as red-hot platinum very rapidly becomes contaminated by alloying with various metallic vapours or by coming in direct contact with impurities. Such contamination at once alters the thermoelectric properties, and causes grave errors. Convenient forms of the platinum-rhodium thermocouple are now supplied by nearly all the leading instrument makers. In order to keep the expense of the fire end as low as possible, the Bristol Company use the platinum and platinum-rhodium couple placed just at the end of the pyrometer tube, but further back, where the temperature is never supposed to exceed 1000°F., they substitute an alloy of inexpensive material of such thermoelectric properties that the resultant effect is as though the entire pyrometer were constructed of the more expensive material. Care must be taken to locate this junction of the inexpensive alloy and also the cold end.

For moderate temperatures iron and nickel have been used extensively in thermocouples. They have an advantage of being cheap and forming a couple of great sensitiveness. From ordinary temperatures up to about 800°F. or 1000°C. the iron-nickel thermocouple is serviceable. For industrial purposes this couple is offered in many forms. Thus the Bristol Company incloses it in an outer protecting tube of iron, which when burnt away may be discarded. Stansfield offers a simple modification consisting of a rod of nickel inclosed in a tube of iron, both metals fitting together at the end. The protecting tube furnishes one end of the junction. A water-cooled cold end completes a simple and effective pyrometer which may be read on any convenient millivoltmeter of approximately 25 mv. range.

The low cost of the Stansfield or the Bristol fire end, compared with furnace operation, would quite warrant a fresh end being used at each heating even were this necessary. There is no doubt of the ultimate deterioration of this couple after prolonged use, but this is not a serious objection owing to the low cost of renewals and the stout character of the fire end.

Recording instruments have been devised for the thermocouple, and many of them are extensively used in industrial work.

The first efforts to record automatically were made by Roberts-Austen, who employed the well-known photographic method. For research work involving rapid temperature changes the method has no equal. The small inertia of the moving system renders it quick to respond to the temperature fluctuations. A spot of light reflected from the mirror of a galvanometer falls on a moving photographic film. Subsequent development reveals the trace.

For industrial purposes various devices have been proposed. A simple one extensively used is to provide the moving galvanometer coil with an arm carrying a pen. This pen is raised slightly off a sheet of paper fastened to a revolving drum or disc. At regular intervals an arm depresses the pen and makes an ink dot, so that the position of the pointer on the scale is recorded by a series of these dots. The Bristol recording mechanism is essentially this, the dots occurring so rapidly, once every ten seconds, as to produce a practically continuous record. The Cambridge Scientific Instrument Company make a thread recorder, which consists of a suspended coil millivoltmeter in which the pointer is automatically depressed by clockwork every minute. This forces an inked thread on to a chart carried by a revolving drum. A similar recorder is sold by Baird and Tatlock.

The cold end, as a source of error in the general use of thermoelectric pyrometers, is often overlooked in the more inexpensive instruments. Many devices have been brought out for correcting the errors due to the cold end. A common one is to have the wires leading from the furnace carried down to the floor by a right-angled join. In this way a more uniform temperature is assured. A water-jacket seems to be quite satisfactory and simple to use. The Bristol Company, however, supply a ' cold end ' compensator which consists of a pair of resistance wires in circuit with the thermojunction. A mercury column expands up a tube containing the wires, and thus short-circuits definite lengths. In this way, when the temperature of the cold junction rises and would produce a smaller reading by reducing the current, the rising mercury cuts out some resistance, and so maintains the current in the circuit at a constant value (*see* Fig. 2).

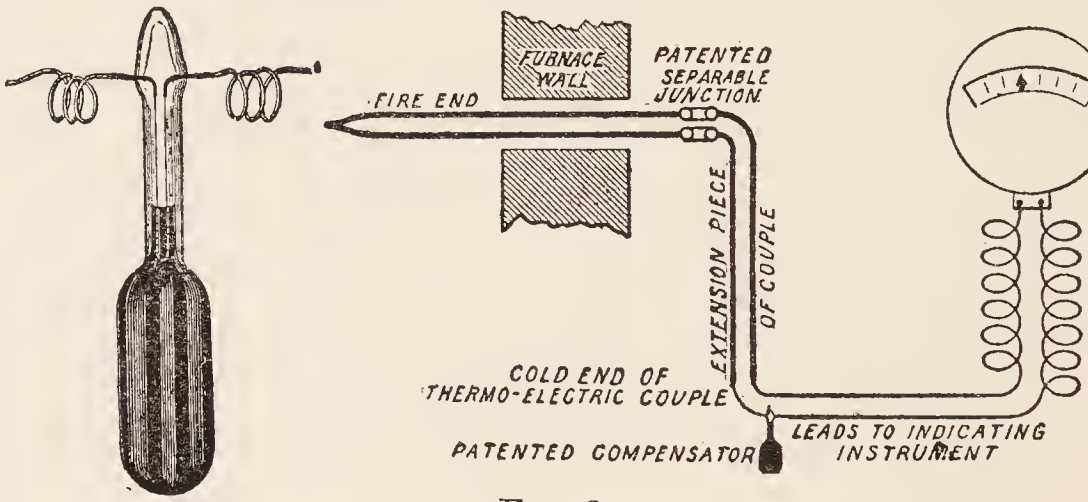


FIG. 2.

There are many ways in which the thermojunction is superior to other forms of electrical pyrometer. It is its own battery, requiring no auxiliary circuits. The fire ends are often cheap and easily replaced, and may be put a long distance away from the furnace. Both indicating and recording instruments may be attached to the same fire end.

Temperatures up to 1600°C. can be measured with simple reading instruments, although even with the platinum-rhodium couples for tem-

peratures higher than 1200°C. continuous heating of the couple is not recommended.

Electrical Resistance Thermometer.

The measurement of temperature by the change in resistance of a platinum wire has been used for many years. The foundation upon which practically the whole of the modern methods rest is the classical work of Callendar in 1887 (Phil. Trans. 1887, A, 178). Not only were the various wires studied, but the simplest way to express the relation between air temperature and resistance changes was suggested. Callendar found that pure platinum was the best wire to use, and that coils of this metal wound on a mica frame would stand temperatures up to 1000°–1200°C. He suggested the platinum scale of temperature, which is given by

$$Pt = \frac{R - R_0}{R_{100} - R_0} \times 100$$

as suitable and reliable for all samples of wire. The relation between the nitrogen thermometer and the platinum scale was given by the expression—

$$t - P_t = \delta\left[\left(\frac{t}{100}\right)^2 - \frac{t}{100}\right]$$

where δ is a constant involving the two constants in the expression connecting the relation between resistance and the air scale. The value of δ for pure platinum wire is found to be 1·50. It changes with the purity a little, being as high as 1·7 for impure wire.

Platinum resistance thermometers are particularly valuable, inasmuch as the nitrogen scale, and through that the standard hydrogen scale can be absolutely defined. For the laboratory no other form of thermometer is so useful, no other thermometer so capable of such precision of reading over so wide a scale, from the lowest attainable temperature up to that of 1000°C. Beyond 1000°C. it is not safe to go. The minute disintegration of the platinum at that temperature very soon causes a change in the resistance of the fine wire coil, and so alters the readings.

There are two methods of reading platinum thermometers. The Wheatstone's bridge method with the compensated leads devised by Callendar, and the potentiometer method as used in Germany.

Of the two methods the former is much more practical. Figs. 3 and 4 illustrate the general plan of connections of the Wheatstone's bridge circuit. The first one shows a short bridge wire BW, with multiple coils r_1, r_2, r_3, &c., and the second shows one long bridge wire on which the whole temperature scale is placed.

The use of the compensated leads in the Wheatstone's bridge method, as shown at C in the diagrams, renders the indications of the thermometer independent of distance. Thus instruments for recording air temperatures have been operated up to a distance of nearly a mile with success.

In the Figs. R_1 and R_2 are ratio coils forming two of the arms of the bridge. B is the battery, G is the galvanometer. In Fig. 4, T is a telephone. In both figures the compensating leads are shown. A galvanometer detector is usually used as a null instrument for obtaining the balance-point, and hence the temperature; but a telephone can be conveniently substituted for the galvanometer without the use of an induction coil to interrupt the current, as in the pyrometer of Tory and Barnes. The make and break of a wire index, which acts as the balance-point finder on the bridge wires, causes the telephone to click at points other than the true balance-point. Callendar has devised a temperature indicator with a galvanometer the deflection of which is proportional to the temperature. This requires a specially connected differential galvanometer, and is not so practical as a null method with moving scale, as is illustrated in the Whipple temperature indicator, or the temperature indicators supplied by Leeds and Northrup in America.

Resistance thermometers lend themselves readily to automatic recording. Such a recorder was devised by Callendar, and is supplied for industrial purposes (*see* Fig. 5). No temperature recording mechanism compares with it for flexibility and accuracy, but it is much

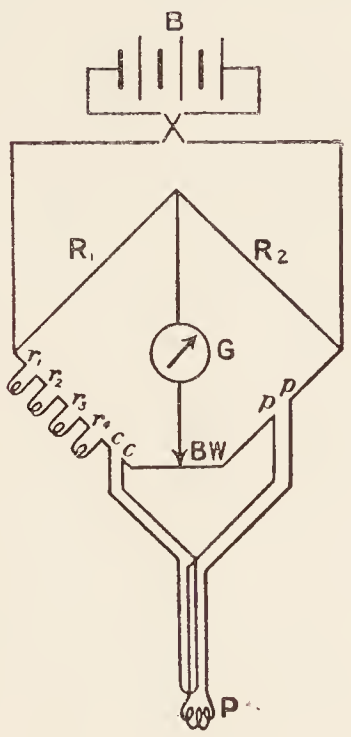


Fig. 3.

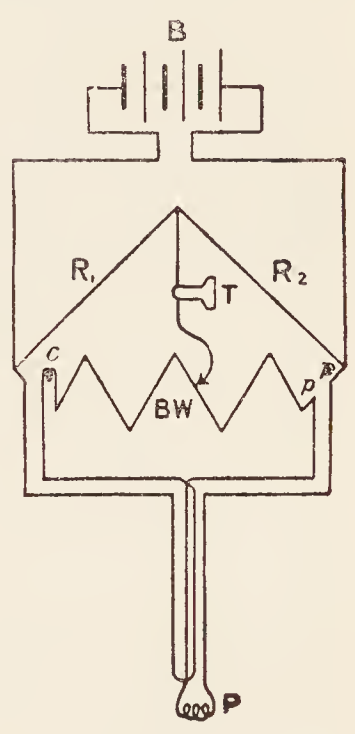


Fig. 4.

less simple than the automatic recorders for thermojunctions. The Cambridge Scientific Instrument Company have perfected the instrument, and now supply it for all classes of temperature work. It consists essentially of an automatic Wheatstone's bridge or potentiometer, as the case may be. A galvanometer G is provided with a special arm *a*, carrying double contacts *dc*, which straddle a contact wheel operated by clockwork C. A right and left-hand relay device, m_2 and m_1, connected with a differential gear, is governed by the double contact. A galvanometer potential sliding contact, SC, is moved over the bridge wire, BW, either to the right or left, as determined by the small swing of the galvanometer engaging one or the other of the double contacts on the contact wheel. The balance is determined by the contact point being moved automatically to the null position by the relay mechanism. Changes of temperature in the pyrometer, P, upset the balance, cause the galvanometer, G, to deflect and the contact, SC, to be moved to a new position of rest. A record is traced on a revolving drum, RD, by a pen

attached to the galvanometer contact, SC. The Wheatstone's bridge connections are shown in Fig. 5, where R_1 and R_2 are the ratio coils, r_1, r_2, r_3, &c., are the multiple coils for the bridge wire. B is the operating battery. *cl* are the compensating leads. *pl* are the pyrometer leads. S_2, S_2, and S_3 are wheels engaging the thread for operating the sliding contact. GW is the galvanometer wire.

While requiring an external battery, platinum thermometers are independent of applied voltage, provided the current through the platinum wire is not large enough to seriously heat the coil. It is often a problem in commercial instruments to obtain sensitiveness with minimum current heating. No satisfactory metal has been found to replace platinum for high temperatures, and hence the fire ends are more expensive than the usual thermoelectric pyrometer.

Optical pyrometers.—For the measurement of very high temperatures the only satisfactory pyrometers so far devised are the optical pyrometers. They are of two classes: those that depend on colour estimation, such as is illustrated most widely in industrial work by the Wanner, and those that depend on the measurement of the total radiation, such as the Féry pyrometer.

Optical instruments are coming rapidly into general use, and extend in range from a low red heat up to the highest attainable temperature. Their great advantage lies in the fact that they are used entirely outside the furnace, and hence suffer no deterioration by the excessive heat, as do all other pyrometers.

In order to obtain the temperature of a radiating body it is necessary to realise that the radiation depends not only upon the temperature, but also upon the emissive power of the radiating body. Of all bodies the radiation and absorption of a black body is the simplest possible, and is taken as the standard. For each temperature and wave length it emits the maximum possible amount of radiation, and it absorbs all the incident energy. For practical purposes a uniformly heated inclosure from which the radiation escapes through a small opening represents most perfectly the conditions of a perfect black body. In such 'black body radiation' it was shown by Stefan, and proved theoretically by Boltzmann, that the total radiant energy was proportional to the fourth power of the absolute temperature, or

$$\int_0^\infty E_\lambda d\lambda = aT^4$$

where E_λ is the energy corresponding to the wave length λ, and the integration includes all wave lengths, and a is a constant. It was shown by Wien that there was a maximum wave length corresponding to each temperature, and that the wave lengths including the maximum were displaced towards the visible region with rising temperature according to a simple law known as Wien's law—

$$\lambda_{max} T = C_1$$

where C_1 is a constant.

Wien also showed that the energy corresponding with the maximum wave length was proportional to the fifth power of the absolute temperature, or $E_{max}\lambda^{-5}=C_2$, where C_2 is a constant. The most complete general equation connecting the energy of any particular wave length with the wave length and temperature has been given by Plank—

$$E_\lambda = C \cdot \frac{\lambda^{-5}}{e^{\frac{c}{\lambda T}} - 1}$$

Wien also gives one, *i.e.*—

$$E_\lambda = C \cdot \lambda^{-5} \cdot e^{-\frac{c}{\lambda T}}$$

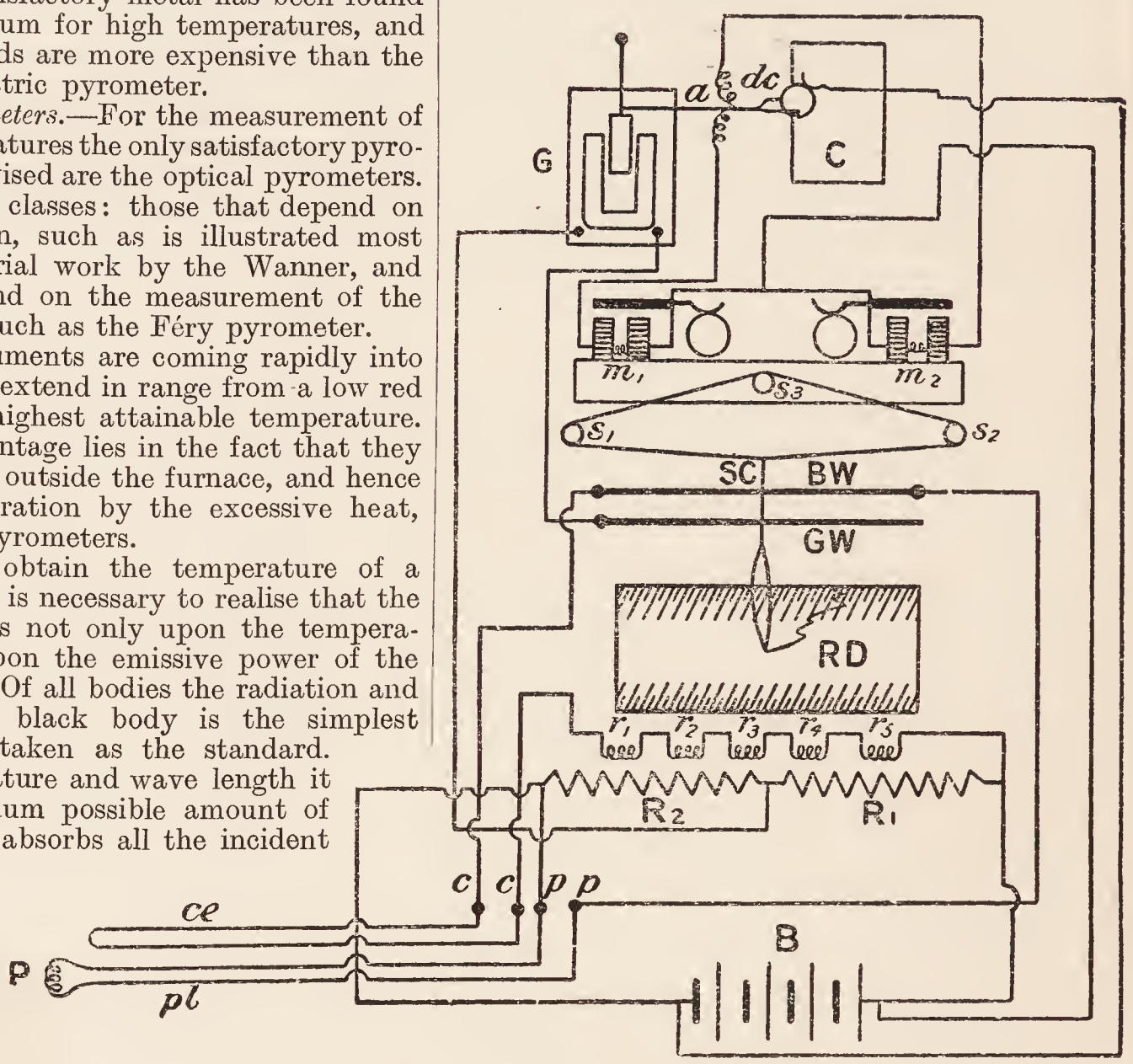


FIG. 5.

which corresponds to shorter wave lengths in the visible region. From this formula we may write—

$$\log E = K_1 + K_2 \cdot \frac{1}{\tau}$$

where K_1 and K_2 are constants, which gives a linear relation between the energy corresponding to any particular wave length and the absolute temperature.

The simplicity of this relation is the basis for calibration of pyrometers making use of the variation of the intensity of some particular wave length, usually a narrow strip in the red, with temperature. Determinations at two temperatures are sufficient to calibrate such a pyrometer.

Inasmuch as all bodies do not radiate as a black body, an optical pyrometer, calibrated

from observations made on a black body, does not read correctly when estimating the temperature of all bodies. The error is not serious, however, for the reason that most bodies are viewed from the interior of a furnace whose sides are usually uniform in temperature with that of the body. In such cases the bodies do not deviate to any appreciable extent from that of a black body.

Polished platinum departs from a black body as much as almost any substance. At 1500°C. the intensity of the light emitted by this substance is only equal to that emitted by a black body at 1375°C. Hence, when viewed in the open by an optical pyrometer measuring the intensity of the red rays, it would appear to be 1375°C., when it was really at the higher temperature. This is expressed by saying that its 'black body' temperature is 1375°C. When this is viewed from the interior of a furnace at 1500°C., polished platinum reflects the equivalent amount of the light which it fails to emit at that temperature as a black body, and in consequence its temperature is measured correctly. Iron fortunately departs to a smaller extent from a black body, and an error of only 30°C. at 1000°C. is made by viewing iron in the open. For many years close estimates have been made by experienced observers of the temperature of a furnace by the eye. The enormous increase in the intensity of light with rise in temperature has made this possible. Thus if the intensity of the red light emitted by a body at 1000°C. be 1, then the intensity at 1500° will be 130 times as great and at 2000° over 21,000 times as great. At about 727°C. the intensity of the light increases 25 times as fast as the temperature. While trained workmen have gained great facility in estimating temperatures, owing to this fact, no accurate gauging of the temperature of a furnace can be made in this way. The eye is too much influenced by the surrounding light and the state of health, to be relied on for uniform results.

Becquerel, in 1862, was the first to use the photometric measurement of the intensity of light as the basis for a system of pyrometry. He compared the red light emitted by a glowing body with that from a standard lamp. The measurement consisted in adjusting the light from the furnace entering the pyrometer until it was equal in intensity with that from a standard light. This is done in the well-known optical pyrometer devised by Le Chatelier (Compt. rend. 1892, 114, 214, 470) by means of an iris diaphragm. The rotation of the diaphragm to reduce or increase the light from the furnace gives the necessary scale for estimating the temperature. In the Wanner pyrometer (Phys. Zeit. 1902, 3, 112; Iron Age, 1904, 18, 24) a polarising devise is used for the same purpose. In the pyromcters of Holborn (Ann. Physik. 1903, 10, 225) in Germany, and Morse (Am. Machinist, 1903) in America, the adjustable scale is supplied not by varying the light from the furnace, but by varying the brilliancy of the electric comparison lamp. Thc filament of the glow lamp is placed in thc field of view of the orifice of the furnace, and the electric current is adjusted until the glowing filament disappears. An ammeter A in series with the lamp and rheostat L supplies the scale for computing the temperature (*see* Fig. 6). In

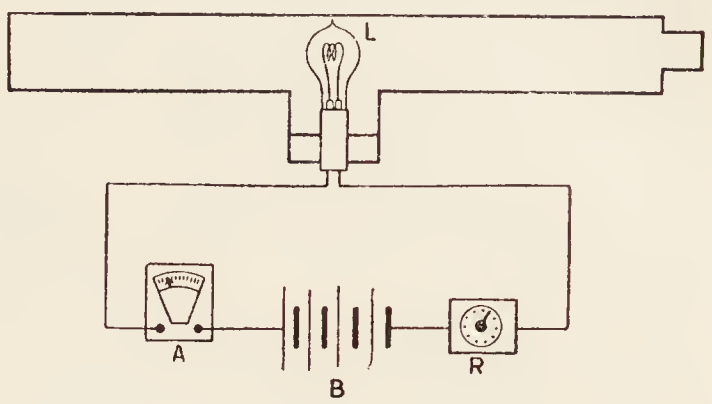


Fig. 6.

all these instruments calibration at two temperatures is sufficient in accordance with the law of Wien.

A very compact form of Wanner optical pyrometer for lower temperatures has been devised, and is sold by Townson and Mercer. This extends in scale from 625°C. to 1000°C. The ordinary form of Wanner extends from 900°C. to 4000°C., smoked glass being used for temperatures above 2000°. For the standardisation of a pyrometer the amyl acetate lamp, as used in photometry, is employed. The comparison lamp of the pyrometer is adjusted to read correctly when the pyrometer is set to view the amyl acetate flame. Pyrometers which are based on Stefan's law of total radiation have been devised by Féry. The best-known is his thermoelectric telescope. In the older type of instrument the rays from a furnace are focussed by a fluorite or large glass lens through a constant aperture on to a small copper-constantan thermoelectric couple. The rise in temperature of the couple is indicated by a galvonometer or millivoltmeter in the usual way. The industrial form of instrument was supplied with a large

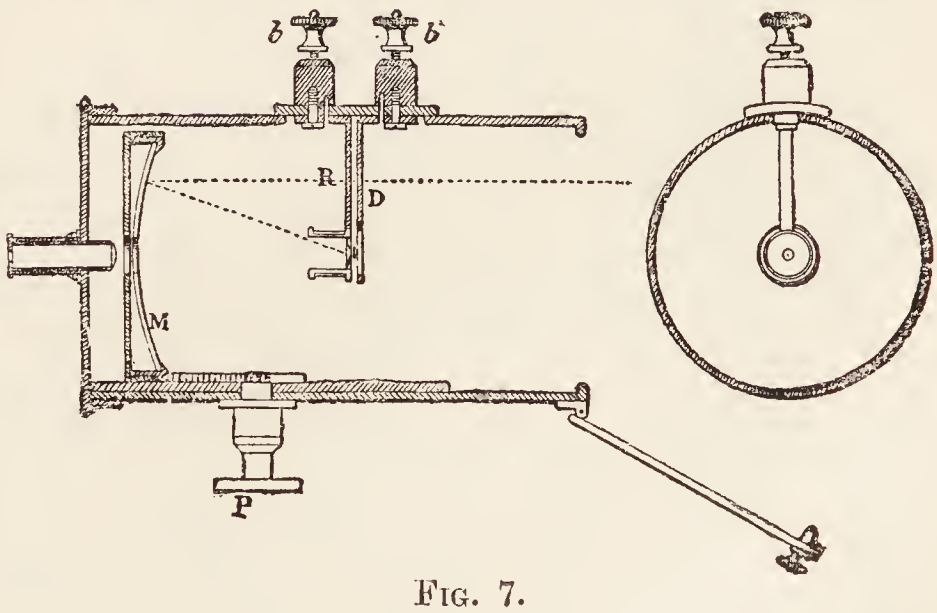


Fig. 7.

glass lens in order to offset the large absorptive power of glass for long heat rays. The instrument is independent of distance provided the entire surface of the thermocouple is covered by the image of the furnace radiation. In order to be sure of this, a focussing arrangement is supplied so that by adjusting the lens the image may be seen to cover the surfacc of the junction.

The modern instruments as now supplied by the Cambridge Scientific Instrument Company are without the lens; a concave mirror at the back of the telescope tube focusses the rays upon the thermojunction (*see* Fig. 7). This is much more accurate, and avoids the selective absorption of the glass. In range the instrument is supplied to read from 500° to 1100°C., 600° to 1400°C., or 800° to 1700°C.; but it may be applied to higher temperatures by using suitable glass absorbing screens.

A recording instrument may be attached to the thermocouple similar in design to those supplied for thermoelectric pyrometers. This is the only optical pyrometer arranged with a continuous recording device. A simpler radiation pyrometer has been devised by Féry, and is similar in design to the thermoelectric telescope. The radiation is, however, focussed on to a small bimetallic spiral instead of the thermojunction (*see* Figs. 9 and 8). A pointer, P, attached to the spiral S moves over a scale, D, calibrated directly in degrees. A focussing arrangement, F, is necessary to ensure the complete covering of the spiral by the image. Thus the instrument is rendered independent of distance. The spiral is very small, measuring only 3 mm. in diameter and 2 mm. wide. This pyrometer is made in three ranges corresponding to those of the thermoelectric telescope, but it is not regarded as so accurate an instrument as the thermoelectric telescope.

There are a number of optical pyrometers met with which are of more or less local importance, but they are all based on the fundamental principles set forth in the description of the forms already discussed. Thus the Féry absorption pyrometer (Figs. 10 and 11) is similar in principle to the Le Chatelier photometric

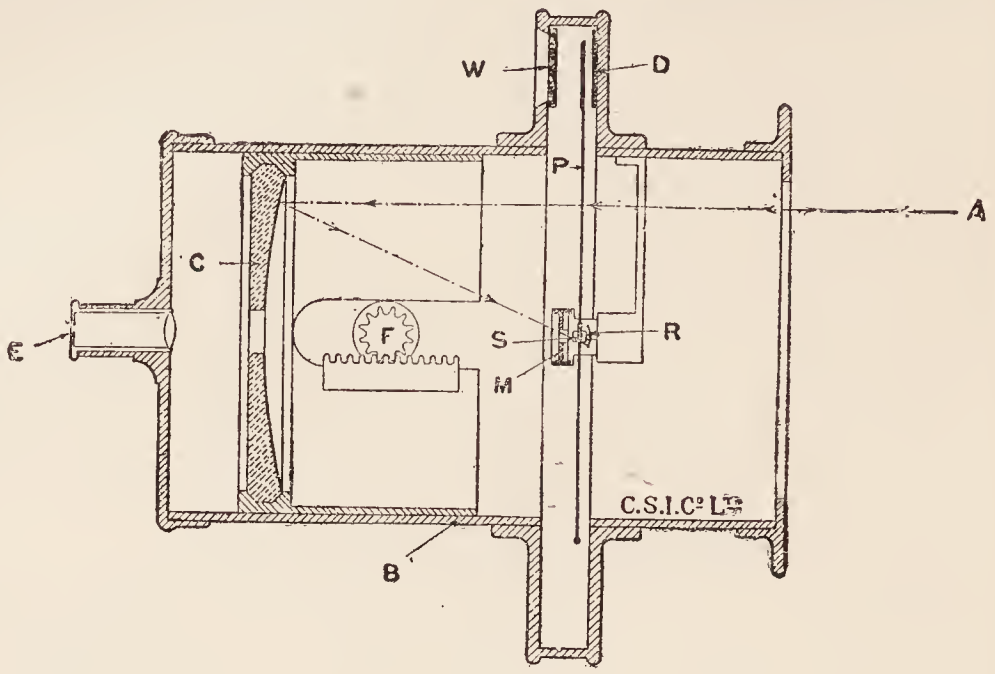


FIG. 8.

pyrometer, except in place of the iris diaphragm for diminishing the light from the furnace two absorbing glass wedges C and C_1 are used. The slipping of the wedges over one another gives a

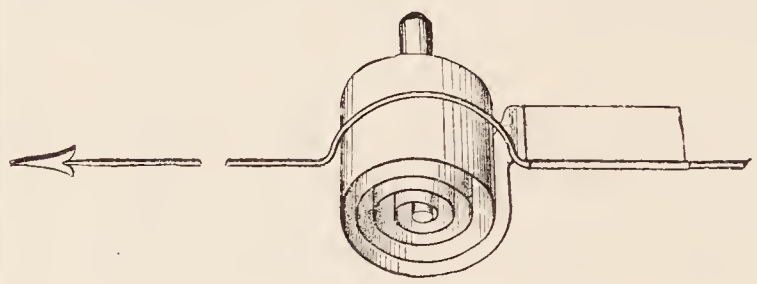


FIG. 9.

sliding scale of an absorbing medium for reducing the light and estimating the temperature.

In Mesure and Nouel's pyrometric telescope the light is polarised by passing through a

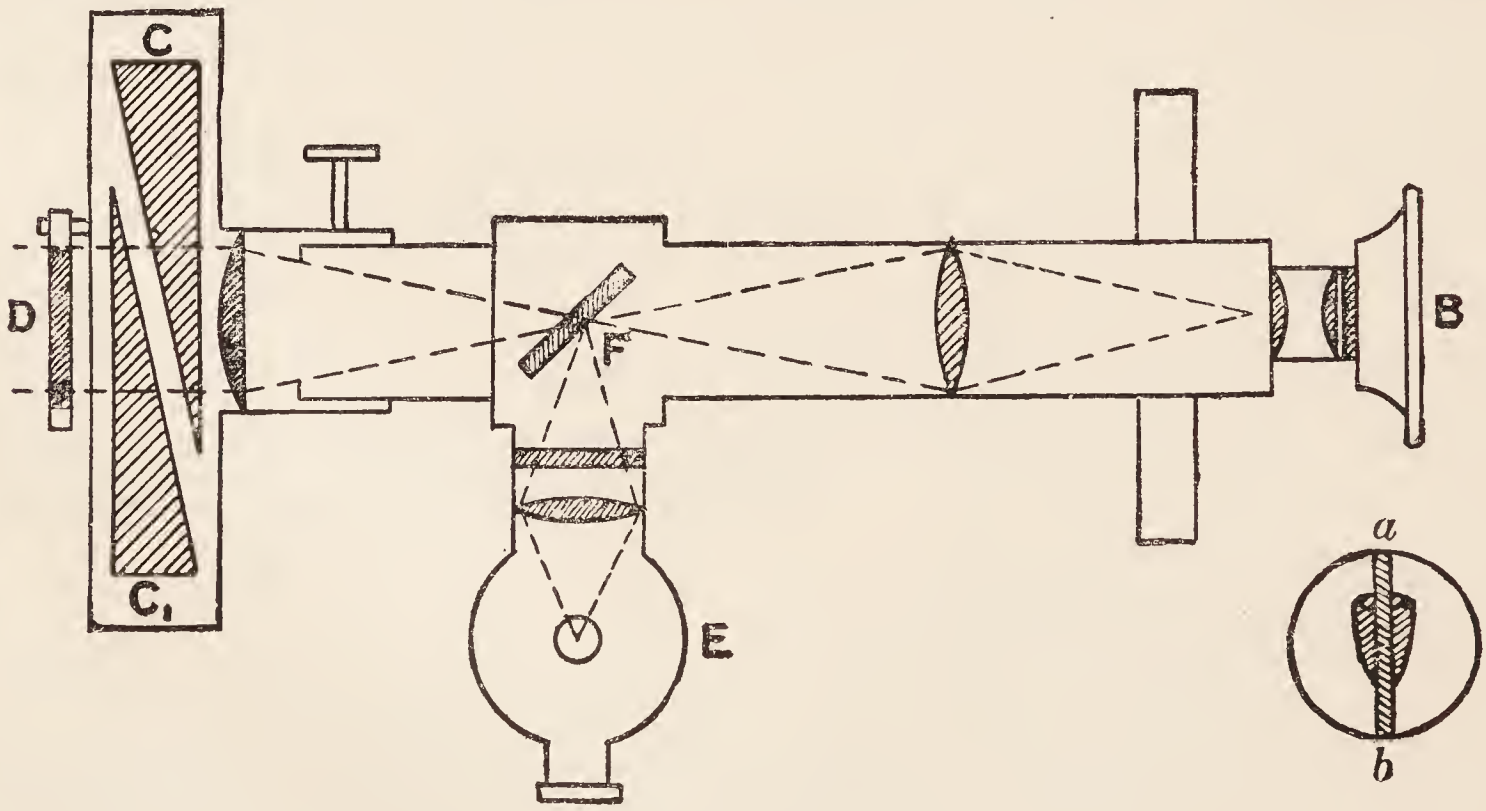


FIG. 10.

Nichol's prism. The light is then passed through a quartz plate cut so as to cause a rotation of the plane of polarisation. A second Nichol serves as analyser. The field of view is coloured because the rotation is inversely proportional to the square of the wave length. The angle between the two Nichols determines the colour that will be seen. A lemon-yellow

colour is taken as being the most sensitive hue to the eye. A change in the temperature causes a change in the composition of the incident light, and hence a change in the colour. By setting to the sensitive hue a scale of temperatures may be established.

Of the large number of pyrometers now offered for industrial work there are certain distinct uses for the various classes into which we have divided the present discussion. The selection of such an instrument must be left to the judgment and disposition of the man in charge of the work. Nearly all pyrometers give trustworthy results when carefully and intelligently used, and the best pyrometers are useless in careless and ignorant hands. So much is saved by economic furnace operation that too much care cannot be taken in the selection of a suitable pyrometer, but it must be understood that a pyrometer alone will not

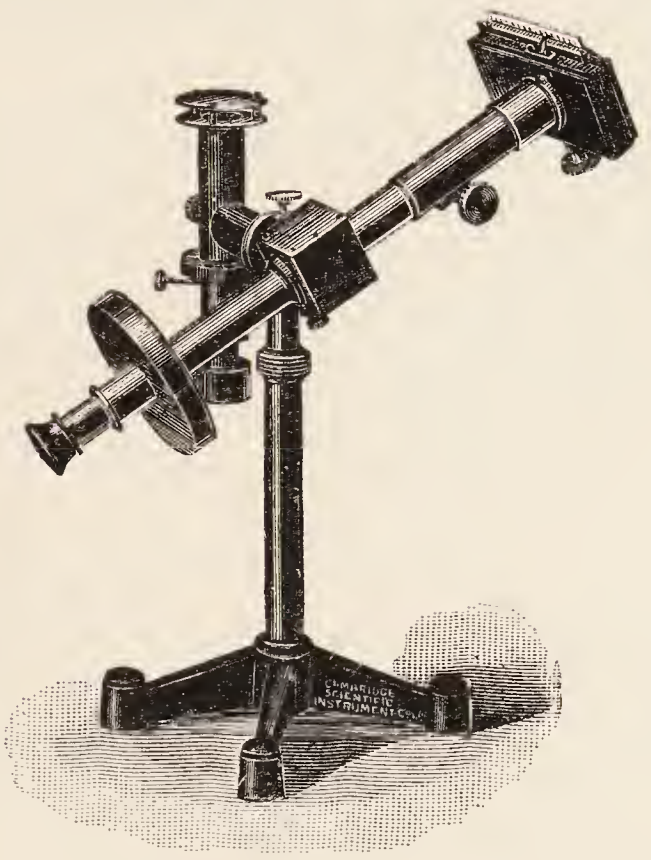


Fig. 11.

serve without the brains to operate and the judgment to interpret.

Bibliography.—Le Chatelier's High Temperature Measurements, translated by Burgess and published by Wiley and Sons, New York; A. Humboldt Sexton's Fuel and Refractory Materials, Van Nostrand and Co.; C. W. Waidner's Methods of Pyrometry; Waidner and Burgess' Optical Pyrometry; A. L. Day and E. E. van Nostrand's Measurement of Extreme Temperatures; the report of the Committee of the Iron and Steel Institute on Pyrometers suitable for Metallurgical work; and many other papers.

Addendum. The values now generally recognised for purposes of standardisation are: water (b.p.) 100°C.; aniline (b.p.) 184°; naphthalene (b.p.) 218°; tin (m.p.) 232°; cadmium (m.p.) 321°; lead (m.p.) 327°; zinc (m.p.) 419°; sulphur (b.p.) 445°; antimony (m.p.) 631°; sodium chloride (m.p.) 800°; silver (m.p. in reducing atmosphere) 961°; gold (m.p.) 1063°; copper (m.p. graphite covered) 1083°; lithium metasilicate (m.p.) 1202°; nickel (m.p.) 1450°; palladium (m.p.) 1550°; platinum (m.p.) 1755°; tungsten (m.p.) about 3000°; carbon arc, about 3500°C.

Thermo-electric pyrometers.—Base metals are used to a very considerable extent for the construction of thermo-couples, due, not only to their comparative cheapness, but to the fact that properly-chosen base-metal couples develop a relatively high E.M.F. Kowalke has shown that base-metal couples are liable to alter if subjected to continual heating, and suggests that such couples should be 'aged' by continued heating before calibration. Carbon and graphite couples are used for temperatures exceeding 1200°C. (Bidwell, Phys. Rev., June, 1914). The potentiometer principle has been largely adopted for commercial instruments.

Resistance pyrometers.—Sir Wm. Crookes has shown that platinum is measurably volatile above 1000°C., and this explains why pyrometers give erroneous readings when continuously used for higher temperatures.

Radiation pyrometers.—Whipple has applied the Féry pyrometer to the determination of the temperature of molten metals by mounting it at the open end of a fire-clay tube, which is dipped into the molten metal, thus keeping the couple in permanent focus.

A type of optical pyrometer depending upon the principle of colour extinction has been introduced. Lovibond has introduced a colour-matching pyrometer which has been found to be very sensitive.

Recorders.—Instruments which give an inked record are taking the place of the photographic recorder of Roberts-Austen (Darling, J. Roy. Soc. Arts, 1915, 63, 590; J. Soc. Chem. Ind. 1915, 34, 600). H. T. B.

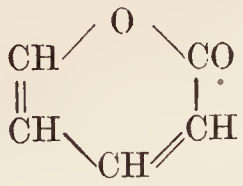
PYROMORPHITE. A mineral consisting of lead chloro-phosphate $(PbCl)Pb_4(PO_4)_3$ or $3Pb_3(PO_4)_2PbCl_2$, crystallising in the hexagonal system and isomorphous with apatite. It is occasionally found in sufficient quantity to be mined as an ore of lead (Pb 76·3 p.c.). The lead may be in part isomorphously replaced by calcium, as in the varieties polysphaerite, miesite, &c.; and arsenic may take the place of phosphorus, thus forming a gradual passage into the chloro-arsenate or mimetite (*q.v.*). The two minerals pyromorphite and mimetite are very similar in appearance, and were formerly included together under the old names 'green lead-ore' and 'brown lead-ore' (Ger. Grünbleierz and Braunbleierz). The name pyromorphite has reference to the fact that fused globules of the mineral on solidification become bounded by a number of minute facets. The mineral usually occurs crystallised; the hexagonal prisms are often somewhat rounded and confusedly aggregated. The colour is usually yellow, brown, or green, and the lustre resinous. Hardness $3\frac{1}{2}$–4; sp.gr. 6·5–7·1.

Pyromorphite is a mineral of secondary origin, and is found, often in association with cerussite, in the upper oxidised regions of veins of lead ore. It has been obtained in many lead mines, perhaps most abundantly in the Friedrichssegen mine, near Ems in Nassau, where in 1868 a crystallised mass measuring $4\times3\times1$ metres was found. Large quantities have also been yielded by the old mines of Huelgoat and Poullaouen in Brittany. It is common at Broken Hill in New South

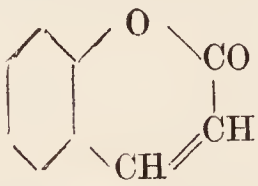
Wales and at Broken Hill in North-Western Rhodesia. L. J. S.

PYRONAL. Trade name for antipyrin salicylacetate.

α-PYRONE or COUMARIN GROUP. Though colouring matters containing the γ-pyrone nucleus are prolific in nature, this is not the case with those containing the α-pyrone grouping—



and indeed but one member of this series, namely daphnetin, has at present been isolated. This is somewhat remarkable, for though coumarin or pheno-α pyrone



which is to be regarded as the mother substance of this class, can only yield a very limited number of hydroxy compounds having tinctorial property, the introduction of phenyl or other groupings into the molecule, as in the case of the γ-pyrone compounds, obviously much increases its possibilities in this respect. Compounds of this type have indeed been synthetically prepared.

The literature referring to coumarin and its derivatives is too voluminous to be given in any detail here, and a brief résumé of those points immediately bearing on the subject of the natural colouring matters can only be dealt with.

Coumarin itself, which occurs in the Tonka bean and in numerous other natural products, is the lactone of *o*-coumaric (*o*-hydroxycinnamic) acid—

$$C_6H_4\begin{matrix}OH\\CH\end{matrix}=CH\cdot COOH$$

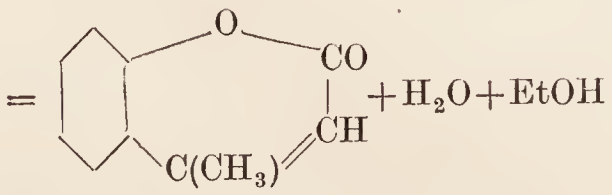
It was first artificially prepared by the late Sir W. H. Perkin from salicylic aldehyde, acetic anhydride, and sodium acetate—

$$C_6H_5COH+CH_3\cdot COONa=C_6H_5CH=CH\cdot COONa+H_2O$$

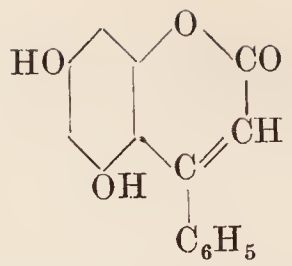
the sodium *o*-cumarate thus obtained passing on acidification into coumarin (*v.* COUMARIN).

Pechmann and Duisberg (Ber. 1883, 16, 2119) synthesised coumarins and hydroxycoumarins substituted in the side chain by the interaction of aceto-acetic ether, or benzoyl acetic ether, with phenols in the presence of dehydrating agents thus—

$$C_6H_5OH+CH_3\cdot CO\cdot CH_2\cdot COOEt$$

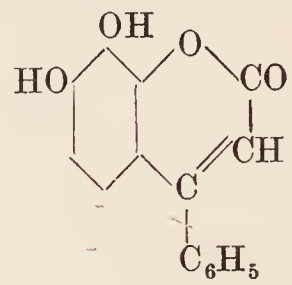


Such a method was also employed by v. Kostanecki and Weber (Ber. 1893, 26, 2906) in the synthesis of a *m*-dihydroxyphenyl coumarin—



from benzoyl acetic cster and phloroglucinol.

In the same way also pyrogallol and benzoyl acetic ester give β-phenyl daphnetin—



This consists of faintly yellow needles, soluble in alkaline solutions with a red colour which dye with aluminium mordanted fabrics a bright yellow shade.

Coumarin forms oxonium compounds, and though itself sparingly soluble in water readily dissolves in concentrated hydrobromic and hydrochloric acid with the formation of the corresponding salts. The unstable *hydrobromide* thus obtained was first isolated by Ebert (Annalen, 1884, 226, 347), and the following compounds of this class have been described by Morgan and Micklethwait (Chem. Soc. Trans. 1906, 89, 863).

Coumarin platinichloride

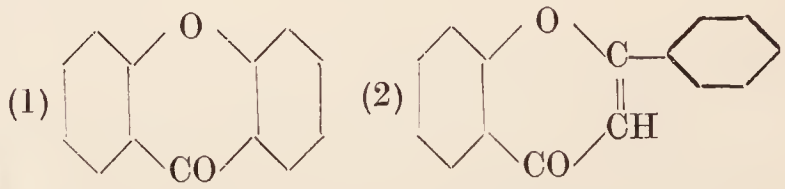
$$C_{36}H_{24}O_8,H_2PtCl_6,4H_2O$$

yellow needles, *C. aurichloride*

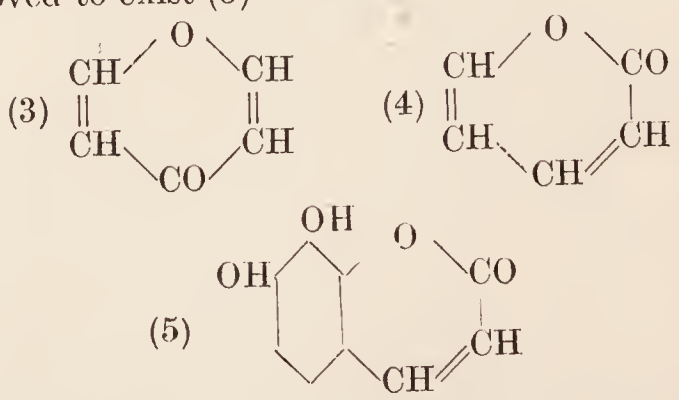
$$4C_9H_6O_2,AuCl_4,4H_2O$$

C. cobalticyanide, $3C_9H_6O_2,H_3Co(CN)_6,3H_2O$, colourless crystalline precipitate, and *C. hydriodide periodide*, $4C_9H_6O_2,HI,I_3$, dark green needles. See also Dox and Gaessler (J. Amer. Chem. Soc. 1917, 39, 114) and Simonis (Ber. 1917, 1137).

The majority of the natural yellow colouring matters are derived either from xanthone (1) or flavone (2)—

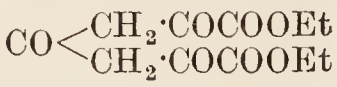


and the general properties of these compounds are due to their possession of the γ-pyrone nucleus (3). Colouring matters, on the other hand, containing the α-pyrone group (4), are as yet but little known, for hitherto only one, *daphnetin*, a dihydroxycoumarin, has been proved to exist (5)—

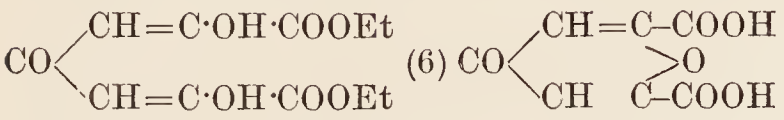


γ-Pyrone itself is the anhydride of a 1 : 5-dihydroxy-3-ketone and has been prepared

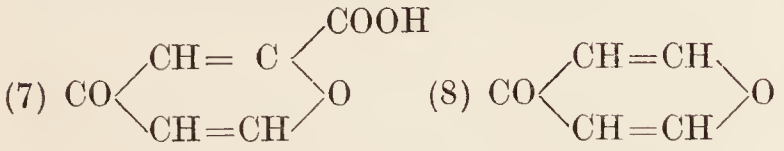
synthetically by Claisen (Ber. 24, 118) from acetone dioxalic (chelidonic) ester—



This on treatment with fuming hydrochloric acid is converted into 2 : 6-γ-pyrone dicarboxylic acid (6)—

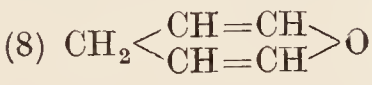


which passes on heating first into comenic acid (7) and subsequently into γ-pyrone (8)—

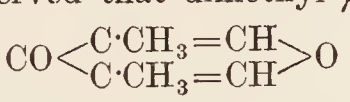


γ-Pyrone is colourless and melts at 32·5°.

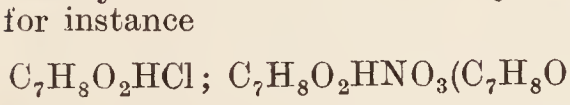
The readiness with which many compounds containing the γ-pyrone or γ-pyran nucleus (8)—



yield with mineral acids well-defined crystalline salts has long been known, having been observed in case of the phthaleins by Baeyer (Annalen, 1876, 183, 1), Fischer (Annalen, 1876, 183, 63), Nietzki and Schröter (Ber. 1895, 28, 50), by Perkin and Hummel, with hæmatein and brazilein (Ber. 1882, 15, 2337), and by Perkin with the flavones (Trans. 1896, 69, 439). These salts, which may be represented as addition products of the dyestuff with one molecule of mineral acid, are in general more highly coloured than the substances from which they are derived, and are, as a rule, very unstable in the presence of water. Various formulæ were at the time assigned to these compounds which appeared to possess a quinonoid structure. Collie and Tickle (Chem. Soc. Trans. 1899, 75, 710), however, observed that dimethyl γ-pyrone—

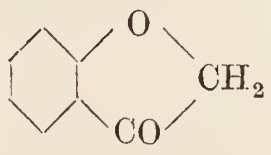


itself yields in this manner crystalline salts, as for instance



and suggested for the first time that their existence is to be ascribed to the quadrivalence of the oxygen atom. The expriments of Werner (Ber. 34, 1901, 33) supported this view, and it was subsequently shown by Baeyer and Villiger (Ber. 1901, 34, 2679) that all classes of organic compounds containing oxygen yield salt-like derivatives with complex acids, though the formation of compounds of this character with simple acids is of rarer occurrence.

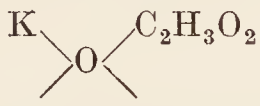
The phenolic colouring matters most distinctly reactive in this respect are those containing a γ-pyrone or γ-pyran nucleus, or an allied grouping, as, for instance, the keto-coumarin (coumaranone) derivatives of Friedländer and Rudt (Ber. 29, 878)—



Not only mineral acids, but also simple organic acids may react in this manner, though the products derived from the latter are less easy to isolate.

With the haloid acids hydroxyanthraquinone derivatives do not appear to give oxonium salts, but the colour change which alizarin and other colouring matters of this group undergo by solution in strong sulphuric acid, is evidence of the formation of the corresponding sulphate. Except in the case of rufigallic acid, which thus forms a beautiful crystalline sulphate, but from which, however, excess of sulphuric acid cannot be satisfactorily removed, no other oxonium salts of the anthraquinone series have as yet been isolated. Oxonium salts of the simple hydroxy ketones with mineral acids are also difficult to prepare.

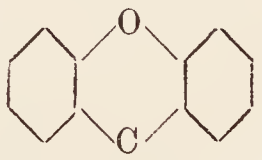
A second reaction, possibly due in its inception to the formation of oxonium compounds, is the behaviour of phenolic colouring matters in general in the presence of alcohol towards the alkali salts of numerous organic acids, more especially those of acetic acid (Perkin, Chem. Soc. Trans. 1899, 75, 433 ; 1903, 83, 130). In this manner the monopotassium salt of the colouring matter is, as a rule, obtained, but in certain cases the reaction does not proceed so far, there being produced an addition compound with the acetate or other alkali organic salt. These latter, which it is suggested are oxonium salts of the type—



may represent the first stage of the reaction in all cases, the compound ultimately suffering conversion with liberation of acetic acid into the mono-alkali salt above referred to. These two reactions have proved of considerable service in the past, not only for the isolation of natural colouring matters, but as an indication of their molecular weight. A. G. P.

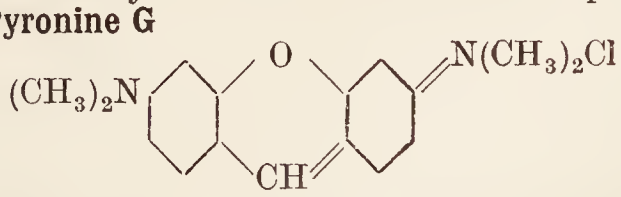
PYRONE DYESTUFFS. This name has been applied to members of the diphenylmethane or xanthene series and the triphenylmethane or phenylxanthene group (*q.v.*).

PYRONINE COLOURING MATTERS. The pyronines contain the pyronine ring

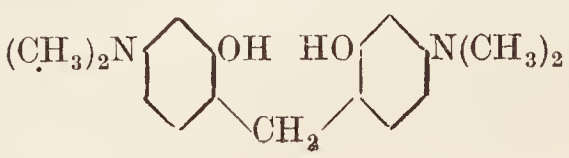


and are derivatives of diphenylmethane. They are obtained by condensing dialkyl-*m*-aminophenols with aliphatic aldehydes or acids, and are bluish-red, fluorescent, basic dyestuffs. They are dyed on cotton mordanted with tannin and antimony and on silk in a neutral soap bath.

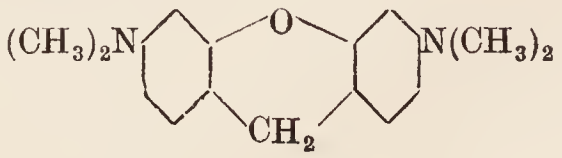
Pyronine G



is prepared by condensing dimethyl-*m*-aminophenol with formaldehyde, whereby dihydroxytetramethyldiaminodiphenylmethane



is produced; by treatment with sulphuric acid this loses water forming tetramethyldiaminodiphenylmethane oxide



which on oxidation furnishes the dyestuff. It forms greenish crystals soluble in water or alcohol with a red colour and yellow fluorescence, and dyes a brilliant bluish-red shade (Eng. Pats. 8673 and 13217 of 1889; 18605 of 1891; D. R. PP. 54190, 58955, 59003, 63081; U.S. Pat. 445684; Fr. Pat. 200401).

Acridine red 3 B is obtained by oxidising pyronine G; it dyes in shades slightly yellower than those given by pyronine (Eng. Pat. 1231 of 1892; D. R. P. 65282; Fr. Pat. 219023).

Literature.—See also Biehringer (Ber. 1894, 27, 3299; J. pr. Chem. 1896, [ii.] 54, 217).

J. C. C.

PYROPE *v.* GARNET.

PYROPHAN. Trade name for a combination of pyrogallol and dimethylamine.

PYROPHANITE. A manganese titanate $MnTiO_3$, found by Hamberg embedded in calcite occurring in the Harstig mine, Pajsberg, Sweden. Crystals belong to the rhombohedral-hexagonal system, and are isomorphous with titanic iron ore $FeTiO_3$; brilliant metallic lustre and deep red tint; powder, yellow with slight tinge of green; sp.gr. 4·537.

PYROPHORIC ALLOYS. In 1903 Welsbach discovered that certain alloys of the rare metals, notably an alloy of iron and cerium, when filed or scratched gave off bright sparks capable of igniting inflammable gases. The original pyrophoric alloy made by Welsbach (ferrocerium) contained about 40 p.c. of iron. Competing products contained as low as 15 p.c. iron, the material being hardened by the addition of 2 p.c. of antimony or bismuth. Silicon is present in nearly all ferrocerium alloys, being contained in the original mixture of rare earth metals (so-called *misch metal*) as an impurity. Some manufacturers add about 5 p.c. of copper to produce a low melting and smooth casting alloy.

An amalgam of mercury and cerium is pyrophoric, and highly explosive; an alloy containing about 25 p.c. platinum is said to possess the greatest pyrophoric properties of any known cerium alloy. Zinc-cerium, and boron-cerium alloys have been recommended as suitable for the ignition of mine lamps. Pyrophoric alloys containing large amounts of carbides are unstable and are readily oxidised.

Misch metal, the raw material for the manufacture of ferrocerium is usually made from the waste from gas-mantle factories after the extraction of the thorium from monazite.

There are two distinct types of lighters on the market. In one the pyrophoric alloy is in the form of a small rod pressed against a hard steel wheel with a roughened surface, the shower of sparks produced by revolving the wheel being projected on a cotton wick impregnated with gasoline. In the other type, a long strip of the pyrophoric alloy is struck by a hard steel pin; the sparks fall upon an asbestos thread saturated with gasoline contained in a reservoir in the body of the lighter.

PYROPHORUS (from the Gk. πῦρ, fire; and φέρω, I bear) is a word which denotes in its widest sense any substance capable of taking fire spontaneously or on very slight elevation of temperature, as is the case with phosphorus, phosphoretted hydrogen, cacodyl, &c. If iron, cobalt, or nickel be reduced by hydrogen from their oxides at a low red heat, the metal is obtained in such a fine state of division as to become incandescent by the oxidising action of the atmosphere; this rapid oxidation is facilitated by the interposition of some infusible material, as alumina or magnesia, between the particles of oxide. When lead tartrate is heated in a glass tube, the lead is left in a very fine state of division, so that if the tube be hermetically sealed, then allowed to cool, the finely-divided particles of lead will take fire immediately on coming in contact with the air when the tube is opened. The reason of this is that the ratio of the surface exposed, when in a fine state of division, to the mass to be heated is so great that the oxidation of the exposed surface is sufficient to bring the mass to incandescence. The sulphides of potassium, sodium, and lithium, obtained by heating the corresponding sulphates with lampblack in a covered crucible, are left in a finely-divided state, mixed with charcoal, and burn spontaneously on exposure to air. Homberg's pyrophorous is obtained by heating alum with lampblack, starch, or flour.

PYRORACEMIC ACID *v.* PYRUVIC ACID.

PYRORETIN *v.* RESINS.

PYROSINE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PYROTARTARIC ACID, and *α-* and *β-iso-* **PYROTARTARIC ACIDS** *v.* GLUTARIC ACID.

PYROTECHNY. The art of making fireworks. Although formerly applied to the smelting and roasting of metallic ores, and to other metallurgical processes involving the use of fire, the term 'pyrotechny' has become narrowed down in modern times so as to include only those effects of fire that are produced mainly for scenic displays. That mixtures of certain substances, some of them more or less familiar, when ignited were capable of producing brilliant and startling effects was known to the early ancients. The art of preparing such mixtures, and of manipulating their mode of combustion, had arrived at a considerable degree of perfection long before the true nature of even the commonest of the materials was known, and before the true principles underlying their use were in the least understood. For these reasons it is that the art of pyrotechny, more perhaps than any other art carried on at the present day, is conducted so largely by 'rule of thumb.'

Pyrotechny is said to have had its origin in the East, firework displays being well known in China for many centuries prior to their introduction into Europe, and even to this day the Chinese and Japanese excel in the production of certain fireworks of great beauty. In Europe pyrotechny was first practised by the Florentines, towards the end of the thirteenth century, at the time that the knowledge of gunpowder began to be diffused among the Western peoples; from Italy the art spread to France, and thence to England and Germany.

Pyrotechny is essentially a 'handicraft'; that is to say, it is one of the very few

remaining arts which is still carried on entirely by hand, and which has not been invaded and revolutionised by the introduction of modern machinery. Even in the largest factory in this country machinery is only employed for wood-working, paper-cutting, and similar operations, and not in the actual making of the fireworks.

Notwithstanding the great variety of effects produced by the many different kinds of fireworks, they all have certain fundamental essentials in common. All fireworks contain a combustible substance, and a supporter of combustion. The combustible, or the *fuel*, may be either one or more of a great variety of substances, such as sulphur, carbon, shellac, resin, pitch, starch, sugar, lycopodium, various picrates, particularly the potassium and ammonium salts; various sulphides, as those of iron, antimony, arsenic; various metals, as iron, antimony, zinc, copper, magnesium, and aluminium.

The supporters of combustion are mainly certain oxygen salts, such as chlorates and nitrates, which are readily able to give up their supply of oxygen to the combustible bodies. The pyrotechnist seldom supplies the fuel with a sufficient amount of the oxygen salt to bring about the complete combustion of the former. The object of the firework-maker is not to discharge into the air the completely oxidised products of combustion, but rather to throw out a certain quantity of material which is in a condition to enter into active combination with the oxygen of the air and to carry on its combustion at the expense of this outside supply of oxygen, many of the combustible substances thus emitted being among the products of the complex chemical reactions which are going forward at the time.

The exact nature of the chemical changes which accompany the burning of a firework are little known. The various mixtures, therefore, which are used to produce certain results have, in most cases, been arrived at, not by processes of scientific reasoning, but by purely empirical rules. Although the art of pyrotechny is regarded as a chemical one, it embraces many mechanical considerations and details which are of no less importance to the production of scenic displays than those which are more distinctly chemical.

For convenience the subject may be subdivided as follows:

1. Preparation of mixtures.
2. Manufacture of cases.
3. Loading of cases.
4. Various accessories, as quick-match, touch-paper, leaders, port-fires.

1. The mixtures used in pyrotechny are called compositions or fuses, and their preparation requires some care. In this branch of the work a knowledge of chemistry is of the greatest importance to the pyrotechnist, in order that he may not only get the best results out of his materials, but also that he may avoid the dangers which attend the use of the highly explosive combinations he has to deal with. Many mixtures also are liable to undergo chemical decomposition, so that they can only be employed when the firework is to be used within a short time of its manufacture. Other mixtures are liable to more rapid spontaneous decomposition, resulting in the ignition and explosion of the materials.

In former days most mixtures were more complex, containing more ingredients than those used at the present time; particularly is this the case with mixtures for coloured effects. This is doubtless due chiefly to the greater purity of modern chemicals, for it is well known that a strontium salt, for example, which contains any quantity of a sodium salt with it will have the crimson colour it imparts to a flame more or less completely masked by the yellow of the sodium. In fact, the purity of the substances used is a point of the highest importance.

The staple materials employed in a great number of fuses are potassium nitrate (known as 'petre'), sulphur, charcoal ('coal'), and meal powder ('meal'). The addition of either 'petre' or 'meal' to a fuse has the effect of making it quicker, whilst the addition of sulphur slackens it; *e.g.* quick-match made from meal, 6 parts; sulphur, 1 part, burns with the greatest violence; whilst that made from meal, 1 part, and sulphur, 1 part, will scarcely burn at all.

The nitre used is always in the form of meal. The sulphur should be crushed lump in preference to flowers; in either case it must be carefully washed free from acid and dried. Most manufacturers avoid the use of 'chemical charcoal,' as it is termed—*i.e.* charcoal which has been made by distillation in retorts for the manufacture of pyroligneous acid. The weighed materials are thrown upon a table, rolled down with a wooden roller exactly resembling a cook's rolling-pin, and thoroughly mixed by being sifted together through sieves. Every pyrotechnist has his own particular formulæ, which are usually kept more or less as trade secrets; the variety of mixtures which are used for the same firework will be seen from the following instances:—

Rockets.

Sulphur	8	1	1	2	4	2	4	8	4	12	1	1
Charcoal	27	2	2	12	8	4	7	11	5	17	2	4
Nitre	36	4	4	20	16	9	16	32	16	50	5	8
Meal powder	6	2	1	1	3	—	—	—	—	—	—	—

Roman candles.

Sulphur	1	2	2	3	3	4	4	7
Charcoal	2	3	3	3	1	1	3	8
Nitre	4	2	9	8	4	5	8	21
Meal powder	3	8	4	3	5	4	8	12

Tourbillons.

Sulphur	1	3	3	7	3	4	4	2	4
Nitre	4	16	5	10	8	17	17	4	8
Charcoal	2	8	3	4	3	4	5	—	—
Meal powder	1	8	11	24	16	—	—	4	9
Steel filings	—	—	—	8	6	—	—	—	—
Cast-iron borings	—	—	—	—	—	6	8	3	4

It is in the preparation of mixtures for colour effects that the purity of the chemicals is of the greatest importance. Coloured stars for shells, Roman candles, rockets, &c., consist of small compacted masses of composition; they are called 'cut' or 'naked' stars, and 'pill-box' stars, according to the method of their manufacture. 'Naked' stars are made by moistening the composition with a solution of either gum, shellac, or with starch, spreading it out upon a slab with a spatula, and marking the surface by cross parallel lines into small squares. When nearly dry, it is broken up by the marks,

and exposed until dry. The rough edges obtained by this method enable the star to ignite readily. Stars made in this way must contain nitre as the oxygen supply, and not potassiun chlorate; for although chlorate mixtures burn more fiercely, they are more difficult to ignite.

The following formulæ are for constructing 'naked' stars, known as 'comet' or 'tailed' stars :—

Sulphur	5	24	2	—	1	2
Nitre	5	24	9	—	10	20
Charcoal	2	8	2	3	6	12
Vegetable black	1	3	3	6	—	—
Meal powder	8	30	6	16	5	7

'Pill-box' stars are made by compressing the dry composition into short cylinders of paper, and inclosing a piece of quick-match for their ignition. These all contain chlorates, as will be seen by the formulæ shown in next column.

The use of copper chlorate is practically inadmissible, on account of its deliquescence, as well as its danger. The well-known substitute

—	Blue stars with sugar					Blue stars without sugar					
Potassium chlorate	8	36	40	6	40	5	40	6	8	2	5
Calomel	4	18	24	5	—	4	20	2	2	—	—
Sugar	5	12	12	4	9	—	—	—	—	—	—
Copper sulphide	3	22	12	—	22	4	20	—	2	—	1
Stearin	—	1	1	—	2	—	—	—	—	—	—
Oxychloride of copper	—	—	3	—	—	—	2	—	—	1	1
Ammonium chloride	—	—	—	—	6	—	—	—	—	—	—
Copper filings	—	—	—	1	—	—	—	—	—	—	—
Shellac	—	—	—	—	—	1	5	—	—	—	—
Sulphur	—	—	—	—	—	—	—	3	4	1	2
Copper oxide	—	—	—	—	—	—	—	1	1	—	—

(obtained by dissolving copper sulphate and potassium chlorate together in water, evaporating to dryness, moistening with ammonia and again drying), called Chertier's copper, although yielding excellent blues, is practically abandoned by manufacturers on account of its liability to explode.

The following formulæ may be used for red, green, and yellow stars :—

—	Red				Green					Yellow			
Potassium chlorate	16	8	16	28	16	8	1	—	6	8	4	12	4
Sulphur	5	6	—	—	5	7	1	1	—	—	—	—	1
Charcoal	1	1	—	—	1	1	—	—	—	—	—	—	—
Calomel	—	—	—	12	—	—	—	—	5	—	—	—	—
Shellac	—	1	—	—	—	2	—	—	—	2	1	3	—
Sugar	—	—	7	12	—	—	—	—	5	—	—	—	—
Strontium nitrate	16	16	—	—	—	—	—	—	—	—	—	—	—
Strontium carbonate	—	—	11	5	—	—	—	—	—	—	—	—	—
Barium nitrate	—	—	—	—	16	21	—	—	7	—	—	—	—
Barium chlorate	—	—	—	—	—	3	2	4	3	—	—	—	—
Sodium oxalate	—	—	—	—	—	—	—	—	—	3	2	8	1

Coloured mixtures are sometimes made up with magnesium filings, to produce specially brilliant stars and asteroids. These vary only slightly from the above formulæ, with the addition of magnesium filings; one illustration of each for red, green, blue, yellow, and white may be quoted. For other coloured fires, *see* BENGAL LIGHTS.

—	Red	Green	Blue	Yellow	White
Potassium chlorate	2	—	5	4	—
Sulphur	2	1	2	—	4
Charcoal	1	—	—	—	—
Shellac	—	3	1	1	—
Calomel	—	—	2	—	—
Magnesium filings	2	2	2	1	2
Strontium nitrate	8	—	—	—	—
Barium chlorate	—	12	—	—	—
Copper oxychloride	—	—	2	—	—
Sodium oxalate	—	—	—	2	—
Potassium nitrate	—	—	—	—	12
Antimony sulphide	—	—	—	—	1

Of late years the metal aluminium in fine powder is largely used either in conjunction with magnesium or as a substitute for it in the above mixtures. Some of these aluminium mixtures have been made the subject of patents, whilst many others are more or less trade secrets. Thus powdered magnesium or aluminium (or mixtures of these metals in varying proportions) mixed with the peroxides of calcium, magnesium, or manganese, along with a suitable quantity of strontium nitrate, gives a very brilliant and rapid red fire. An explosive mixture known as 'Brockite,' patented and manufactured by Messrs. Brock, consists essentially of barium chlorate and aluminium powder. This mixture enters largely into the composition of many fireworks from shells down to the simple cracker. Modern smokeless gunpowder, guncotton, and other high explosives are not employed in pyrotechny.

2. *The manufacture of cases.*—All cases are made of paper, and the selection of the paper is a point of some importance. The paper varies in quality and stoutness, according to the particular kind of firework to be made and to the amount of strain which will be put upon the case. In some instances the material of the paper influences the character of the display produced by a particular firework. For example, the Japanese 'spur fire,' which on burning throws scintillations of a peculiar beauty, owes this quality partly to the special paper of which the case is made, for if the same mixture be introduced into a case made of another paper it will be found to have lost to a large extent the property of throwing out these characteristic scintillations. Most of the papers used are of a superior quality, as it is found that greater

strength can be obtained by the use of a smaller quantity of good paper than by employing more of one of inferior quality; paper which is 'loaded' or adulterated cannot be used. The majority of cases are made of brown paper, although some, and more especially the smaller sorts, as crackers, Catherine wheels, &c., are always made of white cartridge. In a large factory several scores of different papers will be used. The paper is cut to the various sizes required by cutting machinery, and into certain special irregular shapes by dies.

Owing to the great variety in size required, the cases are all made by hand, and, but for slight variations, in the same manner. The tools employed are of the very simplest description, consisting of a wooden or metal roller called the 'former,' and a short wooden board

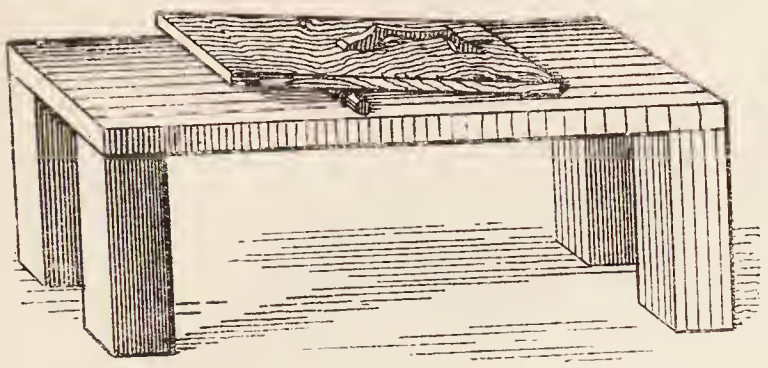


Fig. 1.

with a handle on one side, known as the 'rolling board.' For the larger cases the paper is pasted over its whole surface, and rolled round the 'former,' the operation being done on a narrow slate table. The rolling board is then passed rapidly over it a few times with a firm steady pressure (Fig. 1).

The former is then withdrawn, and the case stood on end until it is so far dry that it can be laid on its side without risk of its losing its cylindrical shape. It is then stacked in a bin in a chamber through which a current of warm air is circulating, in order to render it perfectly dry. In many fireworks the cases have to be partially closed, or constricted near to one end. This is technically known as 'choking.' It may be effected in two ways, either by compressing the walls of the case to the desired extent, or by partially filling the mouth of the case with clay. When the first of these plans is adopted, the operation is performed when the case is freshly made, and only partially dry. For small fireworks it is done by means of a hand lever, made of two blades of steel, and screwed to the edge of the table (Fig. 2).

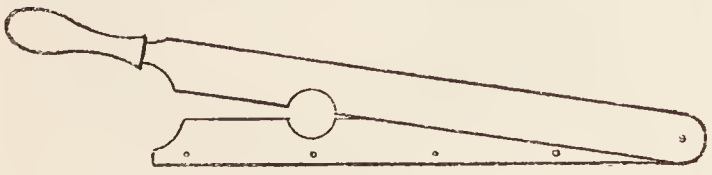


Fig. 2.

For larger cases a foot lever is employed. A noose of cord is looped round the case, one end being fastened to a hook in a wall, or upright post, while the other passes over a wheel to a lever upon the floor, which can be worked by the foot. As the cases have to be choked down to a certain definite orifice, a 'choking-pin' (Fig. 3) is inserted at the time the constriction is being made, which also secures another essential condition, viz. that the choke shall be central. The case is tied round the choke with a string suitable in thickness to the size case, and the whole is then allowed to dry.

When the constriction is effected by means

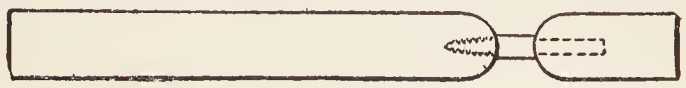


Fig. 3.

of a clay plug, the operation is performed at the time of loading.

For small cases the paper is pasted only along the edges; the former, in this instance a thick metal wire, is placed nearly in the middle of the paper. One end is then folded over nearly to the other, and the double paper rolled over the former (Fig. 4).

The case may be closed at one end by folding the paper in upon the end of the former. These cases require no special drying. Light cases, such as these, are usually made by women, one operator being able to turn out many hundreds in an hour.

Besides cylindrical cases, there are cases made in the form of a sphere, known as 'shells.' These shells, which are constructed of various sizes, up to even 24 ins. in diameter, are made by a process technically known as the 'wet-broke' process. Brown paper of a specially good quality is thoroughly pasted on both

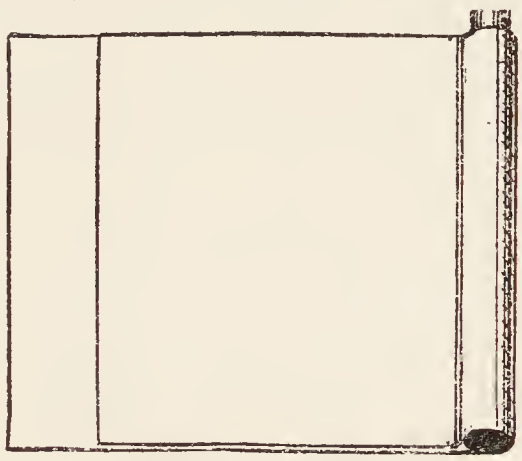


Fig. 4.

sides; strips are then *torn* from the pasted length, and laid upon the inside of a hemispherical bowl or mould, the strips radiating upwards from the centre to the circumference, the ends lapping over the edge of the mould; the workman continues this process until the desired thickness of paper is obtained, which will vary according to the size of the shell from about $\frac{1}{3}$ to 1 in. It is then removed from the mould and allowed to dry, when it presents the appearance shown in Fig. 5. These hemispheres are then placed in a lathe, and the ragged lips or rims carefully turned off. A good workman will so turn out these paper hemispheres that the cut edge shows a most beautiful and perfectly homogeneous section, Two of these hemispheres are securely glued together to form the complete shell. These shells are destined to carry coloured stars, and to be fired from a

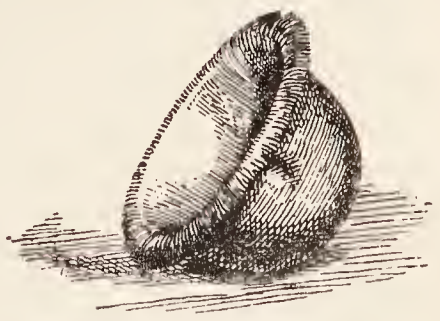


Fig. 5.

mortar; the mould in which they are made has therefore a slightly raised ridge running part of the way down from the circumference, and producing a corresponding indentation, or 'dimple' in the shell, which allows of room between the shell and the side of the mortar for communicating the fire to the propelling charge below.

3. *Loading the cases.*—This operation varies in details according to the special firework to be filled, but, broadly speaking, it may be divided into two sections, viz. *loose-filling* and *ramming*. The apparatus employed in the first of these methods is a metal funnel, of an elongated shape, and a wire, the operation being known as 'wire and funnel' filling. The wire is usually square, and of such a thickness that it will just pass through the end of the funnel. The case to be filled, if a choked case, is placed upon a stand with its choked end fitted upon a nipple fixed for its reception; the nose of the funnel is then inserted into the open end of the case, and by drawing the wire quickly up and down the composition is driven uniformly into the case. When full to the required height, usually determined by a mark upon the wire, the case is closed up. With small fireworks (such as squibs, &c.) this is done by firmly squeezing the end of the case with a tool known as the 'closing-in' machine, and finally dipping the end into a composition, usually red in colour, and technically called 'dip.'

Glue and red lead is the most common mixture for 'dip.'

Long narrow cases (such as are used for crackers and Catherine wheels) are filled without the use of a stand. For the last-named of these fireworks no special tools are required, the long narrow tube being wound by hand upon a small wooden disc, and secured by strips of tape or paper glued across. In the manufacture of crackers two special pieces of apparatus are employed. The first is a rolling or flatting machine. The filled cases are passed between the rollers of this tool, and thereby squeezed flat, the pressure being carefully regulated to the required degree. The other tool is the bending machine. It consists of two upright rectangular brass pillars fastened to a base at such a distance apart as to allow of four of the flattened cases to lie abreast between them (Fig. 6). The cases are bent backward and forward over steel wires about the thickness of a stout steel knitting-needle, until the requisite number of bends is obtained; they are then pressed firmly down with a piece of wood, and removed from the machine. The wires drop out, and are ready for the next set of cases.

The bent cases are then tied up into the familiar compact form with a suitable thread, and the ends primed in the usual way with touch-paper.

Of the second method of loading cases, in which the composition is rammed in, two illustrations may be given, viz. the Roman candle, in which the mixture is gently rammed, and the rocket, in which it is 'malleted.' The case for a Roman candle is a straight or unchoked one. It is placed upon a block, called a 'settle,' the projecting core of which A (Fig. 7) exactly fits into the case.

A small quantity of finely-powdered and sifted clay is first introduced, and tightly driven down by means of the 'rammer,' a wooden rod, which loosely fits into the case. A few smart blows from a mallet upon the head of the rammer will compress the clay into a solid mass, which should occupy about ½ an inch up the case. Fine potters' clay is usually recommended, but London pyrotechnists use the

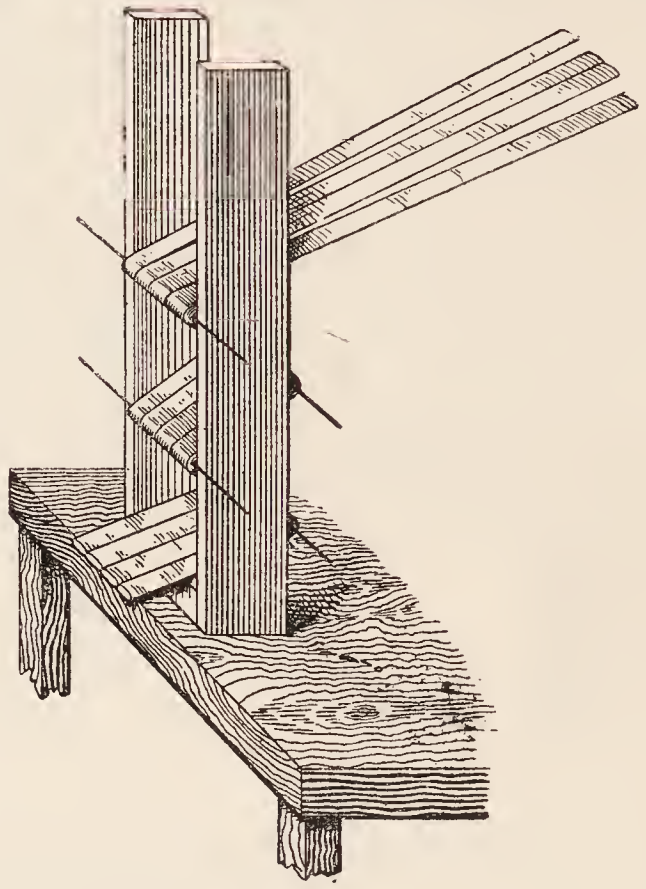


Fig. 6.

common London clay. The use of plaster of Paris instead of clay has been introduced by the Americans, and is said to be much superior. The plaster is mixed with a little water until of about the consistency of soft putty; a pellet is moulded with the fingers, dropped into the case, and gently pressed by the rammer. The case is next to be filled with composition, and coloured stars, alternating. Each layer of mixture is introduced in two quantities, and rammed down by simply 'jumping' the rammer. If more force is applied the stars are liable to be crushed. Care is taken to regulate the charge of mixture, so that each star shall,

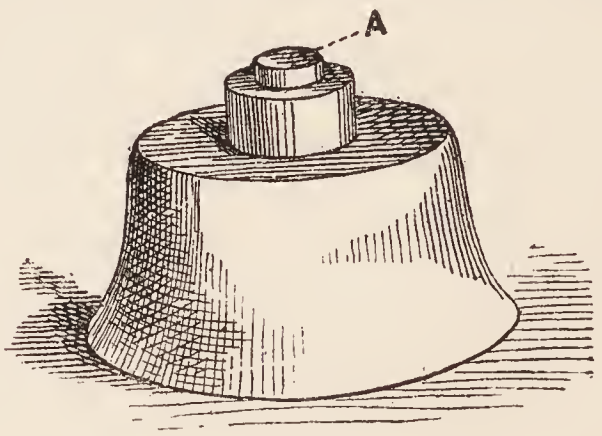


Fig. 7.

as far as possible, be blown out to the same distance. Various devices are adopted to secure the ignition of the star, to prevent it becoming a 'blind star,' as it is termed, one being to make the stars with a hole in them, which is primed with a piece of quick-match.

Rockets are loaded by the mixture being forcibly rammed into the case by a mallet, and as this firework is in some respects of a special

construction, in which the exact relation of all the parts to one another has to be made with much nicety, its construction may be described at greater length. The rocket is a hollow firework, and therefore has to be constructed with special tools. (Very small rockets are often packed solid, and a hole bored up the inside with a common drill.) These consist of a steel conical spindle, or core, firmly screwed into a base of either hard wood or brass, the length and thickness of this spindle varying for each size rocket, a set of wooden rammers, or 'drifts,' of different lengths, and having a cylindrical hole bored nearly up to the head. The number of drifts required for each rocket depends also upon the size; for larger cases four are used. Formerly a 'mould' was employed; this was a strong wooden jacket, to surround the case during the loading operation, to prevent it from splitting; but this is never employed by the manufacturer to-day, owing to improvements in the case-making, resulting partly from the use of better paper. The case to be charged is placed upon the spindle, which must be stood upon a massive wooden or stone block to prevent vibration. It would be quite impossible, for instance, to load a rocket tightly if hammered on a wooden table or floor. If the case has been previously choked by constriction a rammer (technically called the

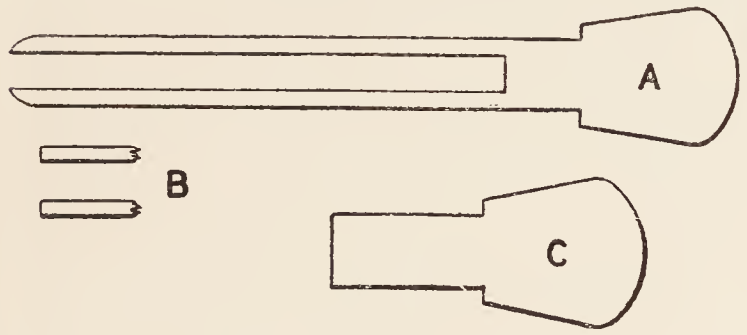


Fig. 8.

'setting-down piece') is introduced, and driven down with a few sharp taps with a mallet: this is to smooth out any wrinkles in the choked end. This 'setting-down piece' A (Fig. 8) resembles the longest 'drift' in all respects except that the end of the latter is cut square, as shown at B, Fig. 8. To prevent the choke from becoming enlarged by being burnt away a small quantity of clay is introduced, and well 'malleted' in with the longest drift, the clay occupying the space shown at CC, Fig. 9. Except in the case of the largest rockets, most manufacturers prefer to use a straight case, and choke it at the time of loading by ramming in a layer of clay, straight cases being easier and cheaper to make than choked ones; with large rockets, however, there is some risk of the clay choke being blown out. Fig. 9, drawn to scale, shows such a case, with the clay choke and spindle. The composition is introduced into the case in 12 equal quantities, measured by a scoop made to hold the exact amount. Each scoopful is malleted well in, the workman being careful to give the same number of blows—usually 18 to 20—and of as nearly equal force as he can judge. As the load rises in the case a shorter 'drift,' with a smaller bore, is used. The length of the longest drift, which must be bored large enough to admit the spindle at *x*, will be 8 times the diameter of the case, exclusive of its head. When the composition reaches one-third up the spindle *y* (Fig. 9), which is known by a mark on the drift, the second drift is brought into use; the ramming is continued with No. 2 until the load reaches *z* (Fig. 9), again ascertained by a mark on the second drift. The third drift loads up to the top of the spindle, when the hollow drifts are replaced by a solid one, C (Fig. 8). The drifts diminish in length by 2 diameters of the case, the three hollow ones being respectively 8, 6, 4, while the solid one is 2 diameters, the 'setting-down' piece being the same length as the longest drift, but with a round end. The case is filled to within about 1 diameter of the top, and then a layer of clay is driven down. The case is removed from the spindle by a gentle twist or turn in one direction only. The nomenclature adopted by the manufacturers to denote various sizes in rockets is the old-fashioned and arbitrary one of 'pounds' and 'ounces'—these weights referring not to the weight of the rocket, but to the weight of a leaden ball of the same diameter as the mould formerly used for loading. As every maker varies in the thickness of his cases, this conveys no exact criterion of the real size of the rocket. By general consent, a case of $1\frac{1}{8}$-in. bore is called a 'pound' rocket, and a $\frac{1}{2}$-in. case an 'ounce' rocket. The following table gives, in a convenient form, the exact sizes of the various parts. The inside diameter is given in eighths of inches, and the relation which should subsist between this measurement and that of thickness of the case, length, and thickness of the stick, will be seen at a glance:—

Inside diameter in eighths	Outside diameter	Length of case in inches	Length of spindle	Diameter of bottom of spindle	Length of stick in inches	Thickness of stick
$\frac{3}{8}$	$\frac{4\frac{1}{2}}{8}$	3	$2\frac{1}{4}$	$\frac{3}{20}$	$3\times8=24$	$\frac{1\frac{1}{2}}{8}\times\frac{1\frac{1}{2}}{8}$
$\frac{4}{8}$	$\frac{6}{8}$	4	3	$\frac{4}{20}$	$4\times8=32$	$\frac{2}{8}\times\frac{2}{8}$
$\frac{5}{8}$	$\frac{7\frac{1}{2}}{8}$	5	$3\frac{3}{4}$	$\frac{5}{20}$	$5\times8=40$	$\frac{2\frac{1}{2}}{8}\times\frac{2\frac{1}{2}}{8}$
$\frac{6}{8}$	$\frac{9}{8}$	6	$4\frac{1}{2}$	$\frac{6}{20}$	$6\times8=48$	$\frac{3}{8}\times\frac{3}{8}$
$\frac{7}{8}$	$\frac{10\frac{1}{2}}{8}$	7	$5\frac{1}{4}$	$\frac{7}{20}$	$7\times8=56$	$\frac{3\frac{1}{2}}{8}\times\frac{3\frac{1}{2}}{8}$
$\frac{8}{8}$	$\frac{12}{8}$	8	6	$\frac{8}{20}$	$8\times8=64$	$\frac{4}{8}\times\frac{4}{8}$
$\frac{9}{8}$	$\frac{13\frac{1}{2}}{8}$	9	$6\frac{3}{4}$	$\frac{9}{20}$	$9\times8=72$	$\frac{4\frac{1}{2}}{8}\times\frac{4\frac{1}{2}}{8}$
$\frac{10}{8}$	$\frac{15}{8}$	10	$7\frac{1}{2}$	$\frac{10}{20}$	$10\times8=80$	$\frac{5}{8}\times\frac{5}{8}$

The stick may be attached to the rocket by being securely tied with string near to the two ends of the case. Modern manufacturers usually bind upon the rocket case a smaller case, just large enough to admit the end of the stick when it has been roughly rounded. Two short spikes are driven into this rounded part of the stick, which, on being thrust up into the case and twisted, cause it to hold very securely. A rocket when laid across the finger should just balance when the point of support is about an inch along the stick, away from the mouth of the case.

The weight of composition required to load

a rocket may be found by the following formula, where d=internal diameter of case in eighths of inches :—

$$\frac{d^3}{9} = \text{number of drachms.}$$

e.g. the charge for a $\frac{2}{8}$ (so-called 'pound' rocket)$= \frac{9^3}{9} = 81$ drachms$=5$ ozs. 1 dr.

Rockets are always made to carry up a load of various combustibles ; these are contained in a slight paper case, known as the 'pot,' which is glued to the head of the rocket. This pot is to be burst, and its ignited contents thrown out, at the moment the rocket reaches the top of its flight, and before it has turned over. The bursting of the pot and the inflammation of its contents are secured by a small quantity of powder, known as 'bursting powder,' the weight of which is usually about $\frac{1}{9}$th the weight of the materials in the pot. This 'garniture' of a

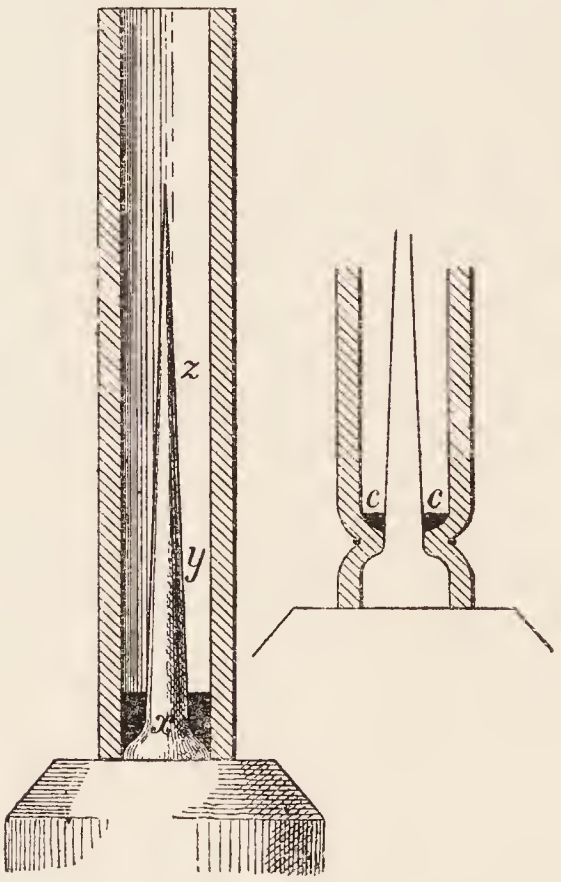


Fig. 9.

rocket may consist of a variety of things, such as gold or silver rain, coloured stars, magnesium or aluminium stars, parachutes, whistling fireworks, &c.

Rockets garnished with parachutes are called 'asteroid rockets.' The parachute is made of thin alpaca, silk, or tissue paper. The latter has to be strengthened by a thread of cotton round its edge, and the paper thoroughly softened by a process of crumpling, to insure the parachute opening when thrown out. Suspended by threads from the parachute is the case, loaded with coloured compositions, usually layers of different mixtures, so that the colour may change as the parachute sails along.

The whistling firework consists of a short paper case, closed at one end, and charged with a composition consisting of potassium picrate 3 parts and nitre 2 parts, or the picrate 15 parts mixed with asphaltum 1 part. The case is not choked, nor is the mouth shaped ; but on ignition the outrushing flames and gas emit a shrill weird whistling sound, gradually rising in a 'crescendo' to a maximum loudness and then falling with a rapid diminuendo. Usually five of these are loaded into a 'pot' to garnish a rocket.

The weight of the load which a rocket can safely be made to carry is the same as that of the composition with which it is filled ; thus a $\frac{2}{8}$ ('pound') rocket can be made to carry up a load of 5 ozs. 1 dr.

An extremely beautiful and brilliant effect is obtained by the use of phosphorus as the 'garniture' of a rocket, but the extreme danger attending the manipulation of this substance has prevented its use by pyrotechnists to any extent. Patents have been taken from time to time with a view to diminish or overcome this difficulty. One of these consists in packing the phosphorus, cut in short sticks of about 1 in., into a perforated paper cage, which has been previously dipped in melted paraffin wax. The cage, with its load, is immersed in a tin can of water until required. When the rocket is ready to be fired, one of these paper cages is taken, the excess of water drained off, and the cage introduced into the rocket pot, into which it just fits. On the bottom of the pot a layer of bursting powder has previously been placed, and covered over with a thin piece of waterproofed paper.

When the phosphorus is introduced the cone is fitted in and the rocket fired.

4. *Touch-paper* is made by impregnating a thin paper—by general consent, blue—with potassium nitrate. The paper commonly employed is 12-lb. double crown. The sheets are spread out and brushed over on one side only with a solution of nitre, containing 1 oz. of the salt to a pint of water. The paper is used for enveloping the live end of fireworks.

Slow-match is prepared by soaking blotting paper in a solution of lead nitrate. Blotting paper is brushed on both sides with a solution containing $2\frac{1}{2}$ oz. of the nitrate to a pint of water. When dry six layers of the paper are pasted together and pressed flat, forming, when again dried, a stiff board. This is then cut into suitable strips with a sharp knife.

Quick-match is made by impregnating cotton with a mixture of starch paste and meal powder. Meal powder is stirred into hot thin starch paste until it has the consistency of paint and is quite smooth. Lamp cotton, with six or eight strands, is then coiled into the vessel containing the 'meal paste,' the cotton being pressed carefully down with a wooden stick to insure its being thoroughly soaked. It is then wound out on to wooden frames, usually about 6 feet high and $2\frac{1}{2}$ feet wide ; these frames are provided with pivots, so that they can be swung upon a support. The frame is turned slowly over and over by one workman, while a second feeds out the cotton through his hand, rounding the wet thread with his fingers as it passes. The frame is then laid down and meal powder sifted first on one side and then on the other ; the cotton is then allowed to dry. When cut it ought to show a perfectly black section. It is preserved in long boxes, as it is necessary to guard it from getting cracked.

Leaders consist of thin paper tubes, through which quick-match is threaded, in order to convey fire rapidly from one firework to another. The tubes have to be such a size as to allow the

match to be introduced without any forcible pushing. The more closely the match fits the pipe the more rapidly does the combustion propagate itself through the length. The pipes are made to any length by slightly pinching the end of one piece and pushing it into the next, the join being bound over with a slip of pasted paper. They can be made to take various angles by cutting away the paper at the elbow af the bend.

Port-fires consist of cases about 10 or 12 inches long, made very thin, usually three or four turns of paper only, and $\frac{3}{8}$ or $\frac{1}{4}$-in. bore, filled with a slow burning mixture—such a nitre 6 parts, sulphur 2, meal powder 1.

One or two technical applications of pyrotechny other than the manufacture of fireworks for spectacular display may be briefly mentioned.

The so-called 'drain rocket' is specially made to emit large volumes of smoke, and often a powerful stench, and is used to detect leaks and stoppages in drains. In so far as it does not travel, but is stationary, the term rocket as applied to it is a misnomer. The 'trawler's flare' is a useful firework to enable fishermen to see the floats and buoys of their nets by night. It consists of a case about 4 ins. long and 1 in. diameter, filled with a flaring mixture, and attached to a wooden handle. An ingenious device is adopted to enable the men to light them in wind and rain. When the cases are loaded a small quantity of chlorate of potash mixture is spread on the end; this is then papered over, a strip of tape being laid under the paper and its end left projecting as a little 'tab' against the side of the case. The handle is bored out, and into the hole fits a little wooden stopper or plug, the tip of which has been coated with red phosphorus. To ignite the flare the sailor pulls the tab and peels off the paper covering, and rubs the end of the wooden stopper across the mouth of the firework, when the mixture is inflamed.

A modified form of rocket is used as a means of carrying a thin line to ships in distress round the coast, forming a part of what is known as the 'rocket apparatus.' These rockets are a combination of two rockets in one case, one being a continuation of the other, so that when the discharge of the first compartment has carried the instrument to its full height the second is ignited and gives it an additional impetus, thereby greatly increasing its range.

Another valuable signal, known as the 'sound and flash rocket' (patented by Messrs. Brock), carries as its load an explosive aluminium mixture, which, as the name implies, explodes with a loud detonation and a dazzling flash of light (*see* also FLASH-LIGHTS).

During the Great War, 1914–18, a number of important pyrotechnic devices were developed for military purposes, many of which are due to the late Wing-Commander F. A. Brock, R.N.A.S. Specially designed rockets, fired not in the usual method, but projected into the air from a rifle by means of a blank cartridge, were employed for signalling purposes; sometimes carrying a single brilliant coloured star suspended from a parachute, sometimes a series of colours arranged to code. A somewhat similar contrivance is the 'Very' light, which consists of tars giving a white light of great brilliancy, fired from the 'Very' pistol. Amongst other light-producing contrivances may be mentioned the 'Dover Flares,' of which at a certain period hundreds were used every night by the anti-submarine patrol in the Dover Straits, each capable of giving an illumination of a million candle-power.

Many pyrotechnic devices were employed for producing enormous volumes of smoke: (*a*) black smoke, in which bituminous materials formed the combustibles, used for smoke screens by merchant ships as a protection against submarines; and (*b*) white smoke, for the production of imitation fog to mask the movements of war ships. Of the former contrivances, namely, for producing black smoke, what is known as the 'E' float became a standard store. Details of most of these devices used for military purposes are for obvious reasons carefully guarded secrets. G. S. N.

PYROPHYLLITE. Hydrated aluminium silicate, $H_2Al_2Si_4O_{12}$, occurring either as pearly folia or as compact masses. In its low degree of hardness (H.=1–2), sp.gr. of 2·8–2·9, greasy feel, and general appearance it is strikingly similar to the two corresponding varieties of the mineral talc (*q.v.*, hydrated magnesium silicate $H_2Mg_3Si_4O_{12}$), and, furthermore, it has the same practical applications. In the foliated variety, usually of a pale green colour, the folia possess a perfect cleavage and pronounced pearly lustre, and they are arranged in characteristic fan-like or spherical groups. The compact variety, usually of a greyish or reddish colour, is included with other minerals of similar appearance under the general term agalmatolite (*q.v.*). Compact pyrophyllite sometimes forms large beds, and is quarried for slate pencils and tailors' chalk ('French chalk'), and by the Chinese for small decorative carvings. In the Deep River region, in Moore and Chatham Counties, North Carolina, it forms a bed in slaty rocks with a maximum thickness of 500 feet and extending for a distance of upwards of 6 miles. Large deposits of a similar character are also known in South Carolina and Georgia. On the talc and pyrophyllite deposits of North Carolina, *see* J. H. Pratt (N. C. Geol. Survey, Econ. paper No. 3, 1900), who gives the following analyses: I, yellowish-white, flaky pyrophyllite; II, apple-green pyrophyllite (also traces of CaO, MgO, K_2O in both analyses)—

	SiO_2	Al_2O_3	FeO	Na_2O	H_2O	Total
I.	64·53	29·40	0·67	0·28	5·45	100·33
II.	63·50	28·73	0·84	0·37	5·85	99·29

L. J. S.

PYROXANTHIN *v.* KETONES.

PYROXENE. An important group of rock-forming minerals consisting mainly of metasilicates of magnesium, iron, and calcium. Although crystallised in three systems they all possess a characteristic cleavage parallel to the faces of the prism of about 87°. They form a parallel dimorphous group with the amphiboles (*v.* HORNBLENDE), in which the corresponding angle is about 56°. The principal members of the group are:—

Orthorhombic Series.

Enstatite (*q.v.*) .	$MgSiO_3$
Bronzite . .	$(Mg,Fe)SiO_3$
Hypersthene (*q.v.*)	$(Fe,Mg)SiO_3$

Monoclinic Series.

Diopside (*q.v.*) .	$CaMg(SiO_3)_2$
Hedenbergite .	$CaFe(SiO_3)_2$
Schefferite .	$(Ca,Mg)(Fe,Mn)(SiO_3)_2$
Augite .) .	$Ca(Mg,Fe)(SiO_3)_2$, with
Diallage (*q.v.*)) .	$(Mg,Fe)(Al,Fe)_2SiO_6$
Ægyrite . .	$NaFe'''(SiO_3)_2$
Spodumene (*q.v.*)	$LiAl(SiO_3)_2$
Jadeite (*v.* JADE).	$NaAl(SiO_3)_2$
Wollastonite (*q.v.*)	$CaSiO_3$
Pectolite . .	$HNaCa_2(SiO_3)_3$
Rosenbuschite .	$Na_2Ca_3[(Si,Zr,Ti)O_3]_4$

Triclinic Series.

Rhodonite (*q.v.*)	$MnSiO_3$
Babingtonite	$(Ca,Fe,Mn)SiO_3 \cdot Fe'''_2(SiO_3)_3$
Hiortdahlite .	$(Na_2,Ca)F[(Si,Zr)O_3]_2$

An igneous rock consisting mainly of pyroxenes is known as *pyroxenite*. L. J. S.

PYROXYLIC SPIRIT (*crude Methyl alcohol*) *v.* METHYL ALCOHOL.

PYROXYLINE *v.* PHOTOGRAPHY.

PYRRHOTITE, *Pyrrhotine,* or *Magnetic pyrites* (Ger. *Magnetkies*). Iron sulphide approximating to FeS in composition and hexagonal (or pseudo-hexagonal) in crystallisation. The mineral, however, always contains an excess of sulphur, ranging in composition from Fe_5S_6 to $Fe_{16}S_{17}$ and most frequently being near Fe_8S_9, the general formula being Fe_nS_{n+1}. E. T. Allen and others (Amer. J. Sci. 1912, 33, 193) explain this variation in composition by the solid solution of sulphur in ferrous sulphide, and give the formula as $(FeS)S_x$. Artificial crystals containing 0·41 p.c. of dissolved sulphur have sp.gr. 4·755, and those with 6·04 p.c. (the maximum amount) have sp.gr. 4·520. The meteoric mineral *troilite* (FeS) is regarded as the end member of this series; it contains no dissolved sulphur, having been formed in contact with free iron. The crystals prepared artificially by Allen were of two kinds—orthorhombic α-pyrrhotite formed at higher temperatures ($<225°$), and hexagonal β-pyrrhotite formed at lower temperatures ($>80°$). From a study of the forms, etching-figures, and magnetic properties of natural crystals, E. Kaiser (Centr. Min. 1906, 261) had already suggested that pyrrhotite is really orthorhombic, but that by twinning it shows pseudo-hexagonal symmetry, as is the case in some other substances.

Natural crystals are not of frequent occurrence; they usually have the form of hexagonal plates or scales, less often pyramids. The best are from the Morro Velho gold mine in Minas Geraes, Brazil, where a crystal measuring 5½ inches across has been found. The massive mineral has usually a granular structure; but it sometimes shows a more or less distinct platy structure, due to a parting parallel to the basal plane. It is a more common mineral than is generally recognised, and is often confused with iron-pyrites. Apart from the obvious difference in crystalline form, it is distinguished from this by its characteristic bronze-yellow colour with metallic lustre, which soon tarnishes on exposure to tombac-brown with a dull lustre; by its lower degree of hardness (H.=3½–4½), being readily scratched with a knife and giving a greyish-black streak; by its lower sp.gr. of 4·58–4·64; by its solubility in hydrochloric acid with evolution of hydrogen sulphide and separation of some sulphur; by the fact that it gives off little or no free sulphur when heated in a bulb-tube, whilst in the air it does not burn freely like iron-pyrites; and by its magnetic character. Small pieces are attracted by a magnet, and suitable pieces can be made magnetic with polarity; the magnetic strength is, however, variable in different specimens. (On the magnetic properties of pyrrhotite, *v.* P. Weiss, J. de Phys. 1898–1905.)

Analyses of pyrrhotite frequently show the presence of nickel, often 2–3 p.c. or up to 5–7 p.c. in the Canadian ores; and also small amounts of copper and sometimes cobalt. These are, however, probably present as impurities, since the massive mineral often occurs in intimate association with other metallic minerals, especially copper-pyrites, iron-pyrites, and pentlandite (*q.v.*). The last-named, a mineral rich in nickel, has frequently been detected by metallographic methods on the polished and etched surfaces of pyrrhotite ores. It is the presence of these impurities that give to pyrrhotite its economic value as an ore of nickel, especially in Canada and Norway. The amount of sulphur (38–39 p.c. as compared with 53·4 p.c. in iron-pyrites) is too low for this mineral to be used as a source of sulphur except as a by-product. The non-niccoliferous pyrrhotite deposit in the Silberberg, near Bodenmais in Bavaria, has, however, long been worked for the manufacture, by a weathering process, of iron-vitriol and 'potée.' The latter is an elutriated red iron oxide used locally for polishing mirror glass. At the rich gold mines of Morro Velho in Brazil and Rossland in British Columbia pyrrhotite is of importance as an ore of gold. At Rossland it carries Cu 0·7–3·6 p.c.; Au 0·4–1·2 oz. per ton; Ag 0·3–2·3 oz. per ton.

Pyrrhotite presents several modes of occurrence. The well-developed crystals are found only in mineral-veins and lodes. Here also large quantities of the massive mineral are sometimes found, *e.g.* at Wheal Jane, near Truro in Cornwall, and Kongsberg in Norway. It is frequently present in small quantities scattered through igneous and thermo-metamorphic rocks, even white crystalline marbles being sometimes speckled with scales of pyrrhotite and graphite. Larger deposits occur in gneiss and crystalline schists near their contact with granite, *e.g.* at Bodenmais in Bavaria, Sulitjelma in Arctic Norway, and Röros in central Norway; these, however, contain little nickel, although the Norwegian are rich in copper. The rich niccoliferous pyrrhotites of Evje in southern Norway and the Sudbury district in Ontario occur as magmatic segregations around the margins of basic igneous rock-masses (gabbro and norite). Much has been written on the deposits of this type: *e.g. see* J. H. L. Vogt, Zeits. prakt. Geol. 1913, 1; 1914, 2; A. P. Coleman, The Nickel Industry, with special reference to the Sudbury region, Ontario, Dept. Mines, Ottawa, 1913; Nickel Deposits of the World (Royal Ontario Nickel Commission, 1917), Toronto, 1917; C. F. Tolman and A. F. Rogers, A Study of the Magmatic Sulfid Ores, Stanford University, California, 1916. L. J. S.

PYRROL BLACK. Pyrrol black is obtained by oxidising pyrrol in an acetic acid solution

chilled with ice, by means of hydrogen peroxide. It is insoluble in most solvents, but is sparingly soluble in pyridine, and very similar to the melanins of animal pigments both in composition (C. 60·01 ; H. 4·87 ; N. 15·91 p.c.) and in properties, and, like them, is soluble in solutions of alkalis and ammonia (Angeli and Alessandri, Gazz. chim. ital. 1916, 46, 279, 283 ; J. Soc. Chem. Ind. 1917, 36, 210).

PYRROL-DERIVATIVES and **DYESTUFFS** *v.* Bone oil.

PYRROLINE *v.* Bone oil.

PYRUVIC ACID, *pyroracemic acid*

$$CH_3{\cdot}CO{\cdot}CO_2H$$

An acid formed by the distillation of tartaric acid and of cream of tartar ; also formed by the distillation of glyceric acid or by oxidising lactic acid by means of potassium permanganate ; by the photochemical decomposition of lactic acid (Ganassi, Boll. Chim. Farm. 1909, 48, 785 ; Zentr. Biochem. and Biophys. 1911, 11, 378) ; by the action of micro-organisms on malic acid (Beyerinck and Folpmers, Proc. K. Akad. Wetensch. Amsterdam, 1916, 18, 1198) ; by the biochemical oxidation of lactic acid by *amylomyces Rouxii* and other moulds (Mazé and Ruot, Comptes rend. Soc. Biol. 1916, 79, 706) ; by the complete hydrolysis of protein substances such as hair (Mörner, Zeitsch. Physiol. Chem. 1904, 42, 123) ; by the oxidation of acetone with permanganate in alkaline solution (Fournier, Bull. Soc. Chim. 1908, [iii.] 259), or with 20 p.c. hydrogen peroxide (Pastureau, Compt. rend. 1905, 140, 1591) ; and by other methods (Baumann and Preuss, Zeitsch. physiol. Chem. 1881, 5, 322 ; Sandmeyer, Ber. 1887, 20, 641 ; Otto, *ibid.* 1894, 27, 838, 1264, amongst others). It is a product of the life of yeast (Fernbach and Schoen, Compt. rend. 1913, 157, 1478 ; *ibid.* 1914, 158, 1719), and is formed in alcoholic fermentation (*v.* Fermentation) (v. Grab, Ann. Bras et Dist. 1922, 20, 203 ; Fernbach and Schoen, *ibid.* 1922, 20, 182). It has been prepared synthetically by the action of hydrochloric acid on acetyl cyanide (Claisen and Shadwell, *ibid.* 1878, 11, 1563). Thus

$$CH_3COCl+KCN=CH_3CO{\cdot}CN+KCl$$

$$CH_3CO{\cdot}CN \xrightarrow{HCl} CH_3CO{\cdot}CO_2H$$

this being a general method for the preparation of ketonic acids. It is, however, best prepared by distilling 500 grms. tartaric acid with 780 grms. commercial potassium hydrogen sulphate in a copper retort lined with asbestos and water-glass. The distillate, which is collected in a well-cooled receiver provided with an upright condenser, is then fractionated under reduced pressure (Wohl and Maag, *ibid.* 1910, 43, 2188 ; *see* also Erlenmeyer, *ibid.* 1881, 14, 320 ; Simon, Bull. Soc. Chim. 1895, [iii.] 13, 335).

Properties.—Pyruvic acid is a liquid, b.p. 59°–60°/12 mm., 165°/760 mm., solidifies at a low temperature ; sp.gr. 1·2649 at 25°, 1·2881 at 4° ; readily soluble in water, alcohol, or ether. It tends to polymerise on standing (Wolff, Annalen, 1899, 305, 156). It combines with nascent hydrogen to form lactic acid (Rockwell, J. Amer. Chem. Soc. 1902, 24, 719 ; Tafel and Friedrichs, Ber. 1904, 37, 3187).

Pyruvic acid has all the properties of a ketone, yielding an oxime, hydrazone (m.p. 192°), addition product with hydrogen cyanide, &c.

When heated alone to 170°, or with acids to 100°–150°, carbon dioxide is evolved, and a variety of products are formed (Hanriot, Bull. Soc. chim. 1885, 43, 417 ; *ibid.* 1886, 45, 81 ; Perdrix, *ibid.* 1900, [iii.] 23, 645 ; De Jong, Rec. trav. chim. 1901, 20, 81 ; *ibid.* 1902, 21, 191 ; *ibid.* 1903, 22, 281 ; *ibid.* 1904, 23, 147). With hydrogen peroxide it forms acetic acid and carbon dioxide (Holleman, *ibid.* 1904, 23, 169). When boiled with concentrated sodium hydroxide it yields oxalic acid.

Pyruvic acid combines with hydrocarbons (Böttinger, Ber. 1881, 14, 1595) ; with urea and urethane (Simon, Compt. rend. 1901, 133, 535, 587 ; *ibid.* 1903, 136, 506 ; *ibid.* 1906, 142, 790) ; with benzaldehyde (Erlenmeyer, Ber. 1901, 34, 817 ; Lubrzynska and Smedley, Biochem. J. 1913, 7, 375 ; phenols (Böttinger, Ber. 1883, 16, 2071) ; with hippuric acid (Erlenmeyer and Arbenz, Annalen, 1904, 337, 302), and with other substances. Tri-iodo pyruvic acid $C_3H_3O_4I_3$, prepared by treating pyruvic acid with iodic and hydriodic acids, forms lemon-yellow crystals with a slightly pungent odour, m.p. about 97° (Garino and Zunini, Gazz. chim. ital. 1922, 52, ii. 220). For other compounds, *see* Garino, Gazz. chim. ital. 1922, 52, ii. 207 ; Garino and Muzio, *ibid.* 1922, 52, ii. 226.

The bacteria which are capable of fermenting dextrose, such as *B. coli*, *B. paratyphi-B*, &c., are also able to ferment pyruvic acid with evolution of carbon dioxide and formaldehyde.

Tests.—In addition to the ordinary ketonic tests, 1 c.c. of the acid may be added to an equal bulk of ammonia solution, when a few drops of sodium nitroprusside are added a violet-blue colour is formed, which becomes more and more greenish as the solution is diluted ; when heated the colour fades slowly to an orange-red, and on boiling it disappears altogether. The only other substance which gives this reaction is acetophenone, which can be distinguished from it by Legal's reaction (Simon, Compt. rend. 1897, 125, 534). When 1 drop of pyruvic acid is added to 10 drops of a freshly prepared solution of α- or β-naphthol (0·02 grm. to 0·05 grm.) in sulphuric acid (1 c.c.) of sp.gr. 1·83, and the mixture is warmed gently, a bright red colour is obtained with β-naphthol in the cold, and an intense blue on warming ; if water or alcohol is added, a fugitive yellow colour is produced. With α-naphthol the colour is yellow in the cold, intense orange on warming, and the colour remains on addition of water or alcohol (Alvarez, Bull. Soc. chim. 1905, 33, 716). All fatty amines when added to a mixture of pyruvic acid and sodium nitroprusside produce a deep violet colour, which, on addition of acetic acid, turns blue, and disappears rapidly (Simon, *l.c.*). It may be identified by the formation of its *p*-nitrophenylhydrazone, m.p. 219°–220°, and may be estimated by treating its solution with a measured quantity of phenylhydrazine solution in excess, filtering off the hydrazone and determining the excess of phenylhydrazine (MacLean, Biochem. J. 1913, 7, 611).

Pyruvic acid forms a number of unstable salts, which pass into gummy masses on heating, but are crystalline in the cold (Wolff, *l.c.* ; De Jong, *l.c.* 1901, 20, 365). It also forms esters, amide, nitrile, imino, sulpho and halogen derivatives.

For the physiological properties of pyruvic acid, *see* Pohl (Arch. Exp. Path. Pharm. 1896, 37, 422), Mörner (Zeitsch. physiol. Chem. 1904, 42, 121), Embden and Schmitz (Biochem. Zeitsch. 1910, 29, 423), Mayer (Biochem. Zeitsch. 1912, 40, 441 ; 1913, 55, 1 ; 1913, 49, 486), Tschernorutzky (*ibid.* 1912, 43, 486), Embden and Oppenheimer (*ibid.* 1912, 45, 186 ; 1913, 55, 334), Ringer, Frankel, and Jonas (J. Biol. Chem. 1913, 15, 145), Dakin and Janney (*ibid.* 1913, 15, 177), Karczag (Biochem. Zeitsch. 1917, 84, 225).

The free acid, but not the sodium salt, acts as a strong poison to wheat seeds (Schreiner and Shorey, J. Amer. Chem. Soc. 1908, 30, 1306).

Pyruvic acid can be estimated quantitively by Furth and Charness' method if it be first of all reduced to hadic acid by zinc dust and hydrochloric acid (Jour. Soc. Chem. Ind. 1910, 903 ; *ibid.* 1923, 370A).

Q

QUARTATION *v.* Assaying.

QUARTZ. The most abundant of minerals composing the earth's crust, and one which appears in a greater variety of forms and modes of occurrence than any other mineral. It is anhydrous silica (SiO_2) crystallised in the rhombohedral system, the degree of symmetry being that of the trigonal-trapczohedral class. The crystals, which are often beautifully developed, are usually bounded by a hexagonal prism and terminated by a six-sided pyramid, the latter being in reality a combination of two rhombohedra. The angle between the normals to the prism and pyramid faces is 38° 13′ (*i.e.* the angle of slope of the pyramid is 51° 47′) ; and the rhombohedral angle is 85° 46′, so that when only one rhombohedron is developed the crystals have the appearance of cubes. Specially characteristic features, always of assistance in the identification of the mineral, are the presence of horizontal striations on the prism faces and the absence of a basal plane perpendicular to the prism. With the development of certain, comparatively rare, trapezoidal faces on the corners between the prism and the pyramid, the crystals betray a helical nature which is inherent in their structure. As shown by the disposition of these extra faces, some crystals are right-handed and others are left-handed ; the two kinds, although similar and mirror-reflections the one of the other, are non-superposable—such crystals are said to be enantiomorphous (a similar relation is also shown by crystals of tartaric acid).

The helical structure of quartz is also impressed on the optical properties of the crystals, which are circularly polarising in the direction of the principal axis. When a beam of plane-polarised light traverses a quartz crystal in a direction parallel to the vertical edges of the prism, the plane of polarisation is rotated to the right or to the left, according to whether the crystal is a right-handed or a left-handed one. On this property depends the use of quartz plates, cut perpendicular to the prism edges, in polarimeters and saccharimeters. A plate of quartz 1 mm. in thickness rotates the plane of polarisation of sodium (D) light through 22° and of blue (G) light through 43°. The mineral is optically uniaxial with positive double refraction (refractive indices are quoted below in a footnote).

On the crystal structure of quartz, *see* Huggins, Physical Rev. 1922, 19, 363. The suggested structure obtained by means of the Lewis theory is in accord with Bragg's conclusions. Each silicon atom is surrounded by four pairs of electrons at tetrahedron corners, which act as bonds connecting it to four equidistant oxygen atoms. Each oxygen atom is also surrounded by four tetrahedrally oriented electron-pairs, two of which serve as bonds connecting the oxygen to silicon atoms. *Cf.* Shearer, Proc. Phys. Soc. 1923, 35, 91.

Crystals of quartz possess no distinct cleavage ; they break with a bright and glassy conchoidal fracture, and small fragments have sharp splintery edges. Fractured surfaces sometimes exhibit a minute rippled marking, like the marks made when the thumb is pressed against a plastic surface ; this is especially characteristic of the amethyst variety, and is due to the lamellar intergrowth of right-handed and left-handed quartz. (Sections of such intergrowths exhibit 'Airy's spirals' in the polariscope.) The mineral readily scratches glass, and itself cannot be scratched by steel ; it is selected as No. 7 in the mineralogist's scale of hardness. These characters are of much help for the recognition of the mineral when crystal-faces are not developed. The sp.gr. is 2·65.

Quartz is very resistant to chemical reagents and to weathering processes. For this reason, when rocks are weathered and disintegrated the quartz remains as the ubiquitous quartz-sand. It is insoluble in acids, with the exception of hydrofluoric, and is only slightly attacked by solutions of caustic alkalis (in which hydrated silica and opal are soluble). When fused with sodium carbonate, it yields sodium silicate ; it is slowly attacked by fused borax, but not by microcosmic salt. It is slightly soluble in superheated water and in superheated solutions of sodium silicate and sodium borate (*see* G. Spezia, Atti Accad. Sci. Torino, 1895 *et seq.*, on the solubility of quartz and the artificial growth of quartz crystals).

When quartz is heated it undergoes a series of remarkable changes. In the first place, it usually decrepitates violently, owing to the presence of vast numbers of microscopic cavities containing water and liquid carbon dioxide (W. N. Hartley, Chem. Soc. Trans. 1876, i. 137 ; 1877, i. 241). At 575° there is an abrupt change in the coefficients of thermal expansion, the circular polarisation, and the refractive indices.[1] This change from α-quartz

[1] F. Rinne and R. Kolb (Jahrb. Min. 1910, ii. 138) have made a large number of determinations of the refractive indices of quartz at temperatures ranging from −140° to +765° ; *e.g.* at 23° (α-quartz) for the line D_2, $\omega = 1{\cdot}5442$, $\epsilon = 1{\cdot}5533$, $\epsilon - \omega = 0{\cdot}0091$, and at 580° ($\beta$-quartz), $\omega = 1{\cdot}5328$, $\epsilon = 1{\cdot}5404$, $\epsilon - \omega = 0{\cdot}0076$. Determinations of the birefringence and rotatory power over a wide range of temperature have been made by F. E. Wright and E. S. Larsen (Amer. J. Sci., 1909, 27, 421).

to β-quartz (stable above 575°) is a reversible or enantiotropic one. From etching experiments on basal sections, O. Mügge (Jahrb. Min. 1907, Festband, 181) has shown that the two forms differ in their crystalline symmetry, α-quartz being trigonal-trapezohedral and β-quartz hexagonal-trapezohedral. This has an important bearing on geological problems; and, as shown by F. E. Wright and E. S. Larsen (Quartz as a Geologic Thermometer, Amer. J. Sci. 1909, 27, 421), it is possible to determine whether in any particular instance the mineral has been formed at a temperature above or below 575°. At a still higher temperature (about 870°) the β-quartz is transformed into tridymite (an orthorhombic modification of silica with sp.gr. 2·32). This enantiotropic change takes place but slowly, and is accompanied by a considerable alteration in volume. At about 1670° the material (now cristobalite) begins to melt to an extremely viscous liquid, so that the exact melting-point cannot be determined. The molten material, if not cooled too slowly, consolidates as a glass with sp.gr. 2·213 (A. L. Day and E. S. Shepherd, Amer. J. Sci. 1906, 22, 273; C. Johns, Geol. Mag. 1906, 3, 118; C. N. Fenner, J. Washington Acad. Sci. 1912, 2, 471; J. B. Ferguson and H. E. Merwin, Amer. J. Sci. 1918, 46, 417). For heat of crystallisation of quartz, *see* Rames Chandra Ray, Proc. Roy. Soc. 1922, A, 101, 509.

This vitrified silica or silica-glass (also called quartz-glass; but the terms 'quartz fibres,' 'quartz tubes,' and 'quartz vessels' are scarcely correct, since the material is no longer quartz) possesses certain remarkable properties. It has an extremely low coefficient of thermal expansion, and can consequently be subjected to sudden changes of temperature without cracking; it is highly transparent for ultra-violet rays, and is a non-conductor of electricity even in a moist atmosphere and at high temperatures; it possesses a high degree of elasticity, and is unaffected by many chemical reagents. The material therefore finds many useful applications in chemical and physical apparatus (W. A. Shenstone, Proc. Roy. Inst. 1902, 16, 525; Nature, 1901, 64, 65).

The characters so far considered are the essential characters of the mineral; in its unessential characters it exhibits a remarkably wide range of variation, so much so that at times the essential characters, useful for purposes of determination, may become masked. In size the crystals may range from mere shining specks (producing a drusy effect on rock surfaces) to those measuring a yard in length and diameter and weighing half a ton. The material may be perfectly transparent or quite opaque, splendent or dull, and of almost any shade of colour. Further, in the massive material there may be different modes of aggregation of the crystalline particles; and impurities of various kinds may be intermixed with the quartz substance. For these reasons a large number of varieties of quartz, differing widely in their external appearance, have been from the earliest times distinguished by special names; and it was only with the rise of chemical science that their true nature was determined.

The following more important *varieties* may be mentioned:—

A. Crystallised quartz with vitreous lustre:
- *Rock-crystal* or 'crystal' (the *κρύσταλλος* of the ancients), the purest form of quartz, the crystals being colourless and water-clear ('Marmorosch diamonds,' 'Bristol diamonds,' 'Brazilian pebble,' &c.).
- *Amethyst* (*q.v.*), of a violet colour.
- *Cirtine*, yellow varieties; the 'occidental topaz,' 'Spanish topaz,' &c., of jewellers.
- *Smoky-quartz* and *Cairngorm*, of a smoke-grey, brownish, or black colour.
- *Rose-quartz*, of a delicate rose-red (never found as crystals bounded by faces).
- *Milk-quartz*, white, with milky opalescence.
- *Sapphire-quartz*, of a blue colour.
- *Prase*, leek-green colour.

B. Quartz with enclosures:
- *Avanturine-quartz*, enclosing scales of mica, hæmatite, &c.
- *Cat's-eye* and *Tiger-eye* (*v.* CROCIDOLITE), enclosing fibres of asbestos.
- *Hair-stone*, *Needle-stone*, &c., enclosing needles of rutile, actinolite, &c.
- *Eisenkiesel*, enclosing iron oxide and hydroxides.

C. Cryptocrystalline quartz (Chalcedony), with waxy lustre:
- *Agate* (*q.v.*), with curved bands differently coloured.
- *Onyx* (*q.v.*), with straight bands differently coloured.
- *Carnelian* (or *cornelian*), yellowish-red or orange.
- *Sard*, yellowish-brown.
- *Chrysoprase*, pale green.
- *Plasma*, dark green.
- *Bloodstone* (*q.v.*) or *Heliotrope*, dark green with red spots.

D. Compact varieties, with dull lustre:
- *Jasper* (*q.v.*).
- *Flint* (*q.v.*).
- *Lydian stone* (*q.v.*).
- *Hornstone* (*q.v.*).
- *Buhrstone* (*q.v.*).

Other varieties, partaking more of the nature of rocks, are sand (*q.v.*), sandstone (*q.v.*), quartzite (*q.v.*), vein-quartz, oilstone (*q.v.*), whetstone (*q.v.*), &c.

In its *modes of occurrence* quartz is equally varied. It is an important essential constituent of many of the primary rocks (gneiss, schist, granite, &c.), and with the breaking down of these it enters largely into the composition of the secondary sedimentary rocks (sandstone, &c.). It is a common product of decomposition of silicate minerals, and it is consequently abundant in veins and cavities in altered rocks and as pseudomorphs after numerous other minerals. In mineral-veins it is the commonest of the gangue materials. The several varieties each have, to a certain extent, their own modes of occurrence. For example, rock-crystal is found in veins traversing gneissic rocks and in pegmatite; amethyst is more frequently found in the geodes of weathered basic rocks (melaphyre), although also in granite and in mineral-veins.

The *uses* of quartz are also numerous. Many of the coloured varieties are employed in jewellery as semi-precious stones, for engraving, and for small ornaments of various kinds; and also, to a certain extent, as an ornamental

stone in buildings. Balance weights, pivot supports, agate mortars, &c., are also cut in quartz. The 'Brazilian pebble' of the spectacle maker is clear rock-crystal from Brazil and Madagascar; and the same material is also cut into prisms, plates, and wedges for optical apparatus. As an abrasive agent quartz finds an extensive application in the form of grindstones, millstones, oilstones, whetstones, sand-paper, scouring soap, polishing materials, sand blasts, &c. For the sand blast ground quartz is more efficacious than quartz-sand, since the particles are more angular and sharper. Ground quartz is also used as a wood-filler, in the manufacture of paints (to which it imparts 'tooth') and in filters. The massive white quartz used for grinding is quarried from veins or obtained as a by-product in felspar mining, mainly in the United States, Ontario, and Sweden. The blocks are heated in kilns and fractured by spraying with water, crushed, and then ground in edge-runners or between rollers, either in a dry or wet condition. Quartz and quartz-sand (*v.* Sand) are also largely used in building; in making cements and mortar; in the manufacture of glass and silica-glass, pottery and pottery glazes, ferrosilicon, and carborundum. It is also used to a certain extent as a flux in copper smelting. Blocks of quartz or quartzite are sometimes used for filling acid towers.

References.—For a detailed *résumé* of the literature on the mineralogical characters and occurrence of quartz, *see* C. Hintze, Handbuch der Mineralogie, 1904–6, i. 1266–1445. On its uses as a gem-stone, M. Bauer, Precious Stones, English translation, 1904, by L. J. Spencer. On economic uses, G. P. Merrill, The Non-metallic Minerals, 2nd ed. 1910; B. Dammer and O. Tietze, Die Nutzbaren Mineralien, Stuttgart, 1913, 1, 132–185; and Mineral Resources, United States Geological Survey.

L. J. S.

QUARTZ-PORPHYRY *v.* PORPHYRY.

QUARTZINE. A finely fibrous form of silica, said to differ in its optical characters from quartz and the fibrous silica of chalcedony (A. Lacroix, Min. de France, 1901, 3, 120).

QUARTZITE. A rock composed wholly of quartz and consisting of quartz grains with a siliceous cement. The cementing quartz is in crystallographic continuity with the quartz of the grains. Such rocks have been formed by the metamorphism of sandstones, either by earth pressures or by the intrusion of igneous masses, or simply by percolating water under ordinary conditions. They are usually greyish or brownish, but sometimes snow-white. Sp.gr. 2·56–2·68. The fractured surfaces are smooth, and pass through the grains as well as the cement. Quartzites are of abundant occurrence, more especially in the older sedimentary formations. Well-known localities in the British Isles are Hartshill in Warwickshire, Stiperstones in Shropshire, Holyhead in Anglesey, Durness in Sutherland, Co. Donegal, &c. Owing to the difficulty of dressing, quartzite is not much used as a building stone, but it is employed for heavy engineering work. Being very hard, although somewhat brittle, it is extensively used for road-metal; the Cherbourg quartzite is exported for this purpose. Blocks of quartzite are used in tube mills for grinding. Being a clean and inert material it can be used for cooling surfaces, filling acid towers, &c. In fact, the pure white rock could be put to many of the same uses as quartz.

Other kinds of quartz-rock forming masses of considerable extent are sandstone (*q.v.*), sand (*q.v.*), quartz-schist, and vein-quartz.

L. J. S.

QUASSIA. *Bitter-wood* (*Quassiæ lignum*, B. P.; *Quassia*, U.S. P.; *Bois de Quassia*, Fr.; *Quassiaholz*, Ger.). The wood of *Picræna excelsa* (Lindley), (=*Picrasma excelsa*, Planchon, N.O. *Simarubaceæ*), a large ash-like tree inhabiting the plains and lower mountain slopes of Jamaica and neighbouring islands (*v.* Bentl. a. Trim. 57). Formerly the quassia of commerce was derived from the allied South American tree *Quassia amara* (Linn.), and the wood of this tree is still employed on the continent; it is known as Surinam quassia and is official in the U.S. P. in addition to the first-named species, which is the only one included in the B. P. *Picrasma quassioides* (Benn.) and *Samadera indica* (Gaertn.) also furnish a very similar wood (Pharm. J. [iii.] 2, 644, 654; 20, 41). The intensely bitter taste of the wood of *P. excelsa* is due to the presence of about 0·03 p.c. of a neutral crystalline substance, *quassin*. Compounds possessing similar properties have been isolated from the other trees mentioned; indeed, it was from *Q. amara* that quassin was first isolated by Winckler (Rep. Pharm. 54, 85; 65, 74). It was analysed and further studied by Wiggers, who obtained it from an aqueous infusion of the wood, after separation of pectinous constituents by means of lime or lead carbonate, by evaporation to dryness and extraction with alcohol. The alcoholic solution yielded a crude quassin, which, after purification, assumed the form of white opaque prisms. Dissolved in water, quassin thus obtained gives no precipitate with chlorine, iodine, mercuric chloride, or salts of lead or iron, but forms an insoluble compound with tannin (Annalen, 21, 40).

Improved methods for the preparation of quassin were proposed by Christensen (Arch. Pharm. [iii.] 20, 481), and by Adrian and Moreaux (Rép. de Pharm. 11, 246). Christensen prepares an insoluble tannate directly from a neutralised aqueous infusion of the wood, and this, decomposed by lime or lead carbonate, yields a crude quassin to alcohol. Adrian and Moreaux take advantage of the easy solubility of quassin in alkalis, and extract the wood with water containing alkaline carbonate. The infusion is evaporated and treated with alcohol, when a solution is obtained which, after several processes of purification, yields quassin in crystals.

According to Oliveri and Denaro (Gazz. chim. ital. 14, 1; 15, 6), who employ for its preparation a modified form of Christensen's method, quassin consists of slender colourless iridescent needles, which melt at 210°–211°. It has the formula $C_{32}H_{42}O_{10}$. It is very soluble in alcohol, chloroform, or acetic acid, but nearly insoluble in ether. 100 parts of water at 22° dissolve 0·253 parts of quassin. Heated with hydrochloric acid in a sealed tube, it yields two molecules of methyl chloride and *quassic acid*

$$C_{30}H_{38}O_{10},H_2O$$

a compound melting at 245° and crystallising in

silky needles. Oliveri and Denaro are thus led to regard quassin as a dimethyl ether of quassic acid, $C_{28}H_{36}O_6(COOCH_3)_2$. The composition of the metallic salts of quassic acid also shows that it is dibasic. Oliveri (Gazz. chim. ital. 17, 570), by acting on the acid with hydroxylamine hydrochloride, obtained a *dioxime* $C_{28}H_{38}O_8(C{:}NOH)_2$, in yellow prisms which melt at 228°–230°. The existence of this compound indicates that quassic acid contains two ketonic CO groups. That this is also the case with its dimethyl derivative quassin, is further shown by Oliveri (Gazz. chim. ital. 18, 169) by the formation of a *phenylhydrazine compound*, $C_{30}H_{42}O_8(CN{\cdot}NHC_6H_5)_2$, by the action of that reagent on quassin.

Quassin reduces Barreswil's (Fehling's) solution, but when it is heated with dilute sulphuric acid no sugar is formed. By this treatment it loses a molecule of water, forming an anhydride, *quasside*, $C_{32}H_{40}O_9$. This compound, which is white, amorphous, and bitter, melts at 192°–194° and when boiled with dilute alcohol, takes up again a molecule of water, quassin being reformed. Quassin may also be converted into the anhydride by heating with acetic anhydride, or even by heat alone at 150° in a current of dry air. If bromine be present *tribromoquasside*, $C_{32}H_{37}Br_3O_9$, results. If quassin be heated with acetic anhydride in presence of sodium acetate the dehydration goes further. In this case two molecules of water are removed, and a *second anhydride*, $C_{32}H_{38}O_8$, a white, pearl-like, amorphous mass, melting at 150°–158°, is obtained. Bromine forms with quassin a substitution derivative melting at 155°, *bromoquassin*, $C_{32}H_{41}Br_3O_9$ (?), and phosphorus pentachloride yields *pentachloroquassin*

$$C_{32}H_{39}Cl_5O_9\ (?)$$

a yellow powder melting at 119°. A *nitro derivative* melting at 130° also exists (D. and O.). When quassin is heated with concentrated hydriodic acid and amorphous phosphorus it yields, among other products, *isodurene*, $C_{10}H_{14}$, and a *hydrocarbon*, $C_{14}H_{16}$, which boils at 220°–240° (Oliveri, Gazz. chim. ital. 17, 575).

From the investigations of Massute (Arch. Pharm. [iii.] 28, 147) it would appear that the bitter crystalline constituents of the different trees mentioned at the beginning of this article, although similar, are not identical. By an improved process this observer obtained from the wood of *Q. amara* four bitter crystalline *quassins*, one of which corresponds with the quassin of Oliveri and Denaro. The others are probably methyl derivatives of this with higher melting-points. From *P. excelsa* the same chemist obtained two crystalline compounds which are designated *picrasmins*. They differ in composition from the *quassins*, but appear also to be methyl derivatives or homologues. One of them yields, by the action of hydrochloric acid, *picrasmic acid*, homologous with the quassic acid of Oliveri and Denaro. By extracting crude quassin with ether, Merck (Chem. Zentr. 1895, i. 435) obtained *quassol* $C_{40}H_{70}O+H_2O$ (?) which crystallises in colourless plates melting at 149°–151°. It differs from quassin by its absence of taste.

Quassia is sometimes used as a substitute for hops in beer. For methods of its detection see Dragendorff (Chem. Zentr. 1881, 285, 299); Chapman (Analyst, 1900, 35); and Allen's Commercial Organic Analysis, 1913, vii. 191. It should be remembered that quassia is used in some hop gardens to combat aphis. G. B.

QUASSIC ACID, QUASSIDE, QUASSIN, *v.* QUASSIA.

QUEBRACHAMINE, QUEBRACHINE *v.* QUEBRACHO ALKALOIDS.

QUEBRACHO ALKALOIDS. The bark of *Aspidosperma quebracho* (Schlecht), the 'quebracho blanco' of Argentina, contains several alkaloids. 'Quebracho colorado' 'red quebracho bark' (*Loxopterygium* (*Quebrachia*) *Lorenztii*, Griseb), the extract of which is used in tanning and which is sometimes confused with 'quebracho blanco,' also contains an alkaloid. The alkaloids of 'payta bark' (*Aspidosperma* spp.) are also conveniently considered under this heading.

The alkaloids of 'quebracho blanco' were originally described by Hesse (Annalen, 1882, 211, 249). Of these only two were well characterised, and recent work (Ewins, Chem. Soc. Trans. 1914, 105, 2738) renders it probable that some at least of the other bases described were impure products derived from the principal alkaloid, aspidospermine.

Aspidospermine $C_{22}H_{30}O_2N_2$, needles, m.p. 208°, b.p. 220°/1–2 mm., sublimes at 180° under reduced pressure, $[\alpha]_D^{18}$ −99° (alcohol) −93° (chloroform). It contains a methoxy group and an acetyl group attached to nitrogen, which is removed by boiling dilute hydrochloric acid; a crystalline diacid base *deacetyl aspidospermine*, $C_{20}H_{28}ON_2$, m.p. 110°–111°, b.p. 210°/1–2 mm. $[\alpha]_D^{18}+2{\cdot}8°$, is thus obtained. Both the latter and aspidospermine on treatment with boiling hydriodic acid (Zeisel) give *aspidosine* $C_{19}H_{26}ON_2$, m.p. 244°–245°, a phenolic base, giving very marked colour reactions, reddish-violet with oxidising agents in sulphuric acid solution, greenish-blue to deep red with ferric chloride.

Quebrachine $C_{21}H_{26}O_3N_2$, needles, m.p. 214°–216° (Hesse), 225°–226° (Ewins), is considered (Fourneau and Page, Bull. Soc. Pharmacol. 1914, 21, 7) to be identical with yohimbine (*q.v.*), (*v.* also Ewins, Chem. Soc. Trans. 1914, 105, 2789). The results obtained by these authors have, however, been criticised by Spiegel (Ber. 1915, 48, 2084), and disputed on pharmacological grounds by Filippi (Chem. Soc. Abstr. 1917, 112, 1, 582). It is present in quebracho blanco in very varying amounts, often only in traces.

Aspidospermatine, $C_{22}H_{28}O_2N_2$ (Hesse), crystalline m.p. 162° $[\alpha]_D$ −73·3°, gives no crystalline salts.

Quebrachamine, crystalline m.p. 142° (Hesse), was not further characterised.

Aspidosamine $C_{22}H_{28}O_2N_2$, and **Hypoquebrachine** $C_{21}H_{26}O_2N_2$, described by Hesse, are both amorphous bases giving no crystalline salts, and are probably mixtures.

In addition to the alkaloids mentioned above, Ewins (*l.c.*) obtained from *Aspidosperma quebracho* two crystalline alkaloids: (*a*) m.p. 149°–150°, giving well marked colour reactions similar to those obtained with aspidosine (*v.* above), and (*b*) m.p. 176°–177°, giving no colour reactions. The amounts obtained were,

however, too small to allow of further investigation.

Loxopterygine $C_{26}H_{34}O_2N_2$ (?), was obtained by Hesse (Ann. 1882, 211, 274) from 'quebracho colorado' as an amorphous base giving no crystalline salts. The amount present is very small.

Paytine $C_{21}H_{24}ON_2,H_2O$, crystals m.p. 156°, soluble in organic solvents, sparingly soluble in water, occurs in 'payta bark' (*Aspidosperma* spp.).

Paytamine amorphous, no crystalline salts is said to be isomeric with paytine (Hesse, Ann. 1882, 211, 271). A. J. E.

QUEBRACHO COLORADO. The quebracho colorado are anacardiaceous trees belonging to the genus *Quebrachia*, growing in the northern part of the Argentine Republic, the wood of which constitutes the well-known tannin substance 'quebracho.' It is imported into this country in the form of logs and is employed for tanning, either in the chipped condition or in the form of extract. Their wood is extremely hard, as the name 'quebracho' (axe-breaker) denotes, and its sp.gr. varies from 1·27 to 1·38.

Jean (Bull. Soc. chim. 1880, 33, 6) found that it contained 15·7 p.c. of a tannic acid not identical with that of oak bark or chestnut wood, whereas Procter (Leather Manufacture, 1903, 269) estimates it to contain about 20 p.c. of a tannin yielding reds (phlobophane) and containing catechol and phloroglucinol nuclei. This tannin is somewhat sparingly soluble in water and can only be used in weak liquors, but gives a firm reddish leather.

In order to isolate the tannin, Strauss and Geschwender (Zeitsch. angew. Chem. 1906, 19, 1121) extract the bark first with chloroform and then with alcohol. Addition of water to the alcoholic extract causes the separation of phlobophanes, and from the clear liquid concentrated in a vacuum the tannin is precipitated by lead acetate, the lead salt being collected suspended in water and decomposed with sulphuretted hydrogen. The resulting solution is evaporated to dryness, the residue dissolved in alcohol and poured into ether. Thus obtained it consists of a light flaky mass, which is hygroscopic and becomes sticky on exposure to moist air.

According to Arata (J. 1879, 306), *quebracho tannin* $C_{26}H_{24}O_{10}$ gives *catechol* on dry distillation, with nitric acid *oxalic* and *picric acids*, by fusion with alkali *phloroglucinol* and *protocatechuic acid*, whereas, by the latter method, Nierenstein isolated also *hydroquinone* and *resorcinol* (Collegium, 1905, 65). According to the latter author, the quebracho colorado probably contains three tannins. By treating a cold aqueous extract of the quebracho colorado with bromine, Böttinger (Ber. 17, 1123) obtained a reddish-yellow compound containing 42·1 to 44·5 p.c. of bromine. Neirenstein, who isolated the tannin according to Trimble's method (The Tannins), treated the solution with lead acetate, filtered, and on adding bromine to the clear liquid obtained a precipitate of *monobromoquebrachotannin* $C_{16}H_{14}Br{\cdot}O_8$, which consists of a cinnabar red powder, and on digestion with alcoholic potash gives *isovanillic acid* and *monobromoquebrachylic acid* needles, m.p. 119°–120°.

Strauss and Geschwender (*l.c.*) consider that quebracho tannin is identical with maletto-tannin, and with the tannin from cinchona bark, and ascribe to it the formula $C_{43}H_{50}O_{20}$. With a mixture of acetic anhydride and acetic acid the *acetyl* compound $(C_{30}H_{22}O_{11}Ac_6)_2$, colourless powder, is produced, and a corresponding *benzoyl* derivative $(C_{30}H_{22}O_{11}Bz_6)_2$ can also be prepared.

Quebracho phlobophane, on distillation with zinc dust, yields anthracene (Nierenstein, Ber. 1907, 40, 4575).

According to Arnaudon the wood contains a colouring matter which gives a fine yellow dye, and this has been examined by Perkin and Gunnell (Chem. Soc. Trans. 1896, 69, 1304) and found to be identical with *fisetin*, the colouring matter of young fustic. This compound, which appears to exist in the wood as glucoside, gives on fusion with alkali protocatechuic acid and resorcinol, and may account for the appearance of the latter phenol among the hydrolytic products of the crude tannin itself. According to Perkin and Gunnell, when an extract of the quebracho colorado is digested with boiling dilute acid a small quantity of *ellagic acid* is obtained.

In addition to the tannins above described, the quebracho colorado is the source of the so-called 'quebracho resin,' which collects as a thickened juice in the crevices of the tree. It has been examined by Arata (Chem. Soc. Abstr. 1878, 984), who describes it as easily soluble in alcohol or ethyl acetate, insoluble in benzene. By fusion with alkali it gives *protocatechuic acid* (?) and *phloroglucin*, and by the action of nitric acid, oxalic and picric acids are produced.

A considerable amount of the tannin contained by the quebracho colorado is of a sparingly soluble nature, and is deposited to some extent from a hot aqueous extract on cooling. This product may be rendered soluble by treatment with alkalis or alkaline sulphites and a large quantity of the so-called 'soluble' quebracho extracts are prepared by heating the material in closed vessels with bisulphites, sulphites, sulphides or even caustic alkalis (Lepetit, Dollfus and Gansser, Eng. Pat. 1896, 8582; *cf.* Procter, Leather Manufacture, 338).

The detection of quebracho tannin in presence of other tanning agents may be effected by first extracting the quebracho-tannin with ethyl acetate. Fat free leather, for example, is extracted with alcohol, the alcoholic extract distilled, and the aqueous solution of the distillation residue extracted with ethyl acetate. After distilling off the ethyl acetate the residue is fused with phthalic anhydride and a little zinc chloride, when if quebracho tannin was present, fluorescein is formed (Jablonski and Einbeck, Chem. Zentr. 1921, 92, iv. 75). A. G. P.

QUELLERZ *v.* LIMNITE.

QUERCETAGETIN was isolated from the flowers of the African marigold, *Tagetes patula*, by Latour and Magnier de la Source (Bull. Soc.chim. 1877, [ii.] 28, 237), who state that it also occurs in other varieties of the same plant. In appearance and general properties it is described as resembling quercetin, the colouring matter of quercitron bark, and from this fact, together with its origin, the name quercetagetin is evidently derived. On the other hand, according to these authors, its crystalline form, solubility in 60 p.c. alcohol, and the numbers obtained on analysis indicated that it was distinct from quercetin $C_{27}H_{20}O_{12}$, and it was

considered to possess the formula $C_{27}H_{22}O_{13}$ (anhydrous) or $C_{27}H_{22}O_{13},4H_2O$ (air-dried). A preliminary re-examination of this colouring matter was made by Perkin in 1902 (Chem. Soc. Proc. 18, 75), and it has more recently been studied in greater detail by the same author (Chem. Soc. Trans. 1913, 103, 209). To isolate the colouring matter, which is largely present in the flowers as glucoside, a concentrated alcoholic extract is diluted with water which precipitates a viscous impurity, and this is removed by means of ether. The clear liquid treated when boiling with addition of a little hydrochloric acid deposits after cooling but a small bulk of the colouring matter, and repeated extraction of the solution with ether is necessary for its economical isolation. The crude product thus obtained can be crystallised from dilute alcohol, but for complete purification it is necessary to prepare the acetyl derivative, and after recrystallisation to hydrolyse this in the usual manner.

Quercetagetin $C_{15}H_{10}O_7$, or as crystallised from dilute alcohol $C_{15}H_{10}O_8,2H_2O$, forms pale yellow glistening needles or leaflets resembling quercetin in appearance and melts at about 318°. Very dilute alkali dissolves it with a pure yellow colour, which by air oxidation becomes olive, and finally deep brown, but these changes are not so marked when a stronger alkali (10 p.c.) is employed. Alcoholic ferric chloride produces an olive-green coloration, whereas cold alcoholic lead acetate forms an orange-red precipitate which on keeping becomes yellower and finally develops a green tint. On fusion with alkali protocatechuic acid is obtained, together with a phenolic product which, however, quickly oxidises, and has not yet been identified.

Quercetagetin readily yields oxonium salts with mineral acids, and of these the sulphate $C_{15}H_{10}O_8,H_2SO_4$, fine orange-coloured needles, has been described.

Monopotassium quercetagetin $C_{15}H_9O_8K$ separates as an orange-yellow semi-crystalline precipitate when potassium acetate is added to a solution of quercetagetin in absolute alcohol.

By acetylation acetylquercetagetin

$$C_{15}H_4O_8(C_2H_3O)_6$$

colourless needles, melting at 209°–211°, is produced, and on alkylation employing alkyl iodide quercetagetin pentamethyl ether

$$C_{15}H_5O_3(OCH_3)_5$$

pale yellow needles, m.p. 161°–162°, and quercetagetin hexamethyl ether $C_{15}H_4O_2(OCH_3)_6$, colourless needles, m.p. 157°–158°, can be prepared. Acetylquercetagetin pentamethyl ether

$$C_{15}H_4O_3(OCH_3)_5C_2H_3O$$

melts at 161°–163°.

Quercetagetin hexaethyl ether

$$C_{15}H_4O_2(OEt)_6$$

m.p. 139°–141°, yields oxonium salts with mineral acids in the presence of acetic acid, the sulphate separating in orange needles, whereas the crystals of the hydrochloride possesses a somewhat more yellow colour. This behaviour is analogous to that of quercetin pentamethyl ether (Watson, Chem. Soc. Proc. 1911, 27, 163).

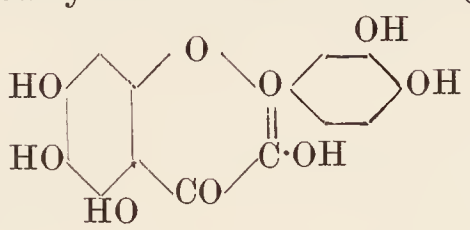
When hydrolysed with alcoholic potassium hydroxide quercetagetin hexaethyl ether gives protocatechuic acid diethyl ether, and quercetagetol tetraethyl ether $C_{16}H_{24}O_6$, which crystallises in prismatic needles, m.p. 46°–48°. The latter yields the oxime $C_{16}H_{25}O_6N$, m.p. 93°–95°, and when oxidised with alkaline permanganate quercetagetinic acid, m.p. 100°–102°, is produced.

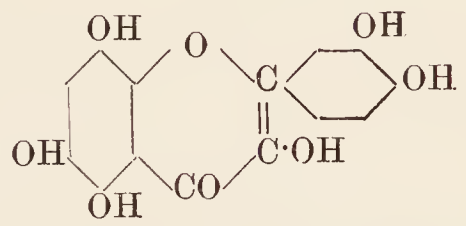
The production of quercetagetol diethyl ether to which the constitution (1) is assigned, the protocatechuic acid diethyl ether (2)

(1) $C_6H(OEt)_3<\begin{matrix}OH\\CO-CH_2\cdot OEt\end{matrix}$

(2) $CO_2H\cdot C_6H_3(OEt)_2$

from quercetagetin hexaethyl ether, indicate that quercetagetin is a pentahydroxyflavonol isomeric with myricetin and gossypetin. Similarly to this latter colouring matter it appears to contain a tetrahydroxybenzene nucleus, and it is suggested that its constitution may be represented by one of the two following formulæ:—





Quercetagetin readily dyes mordanted fabrics shades of a generally similar character to those given by other well-known flavonol colouring matters.

Chromium	*Aluminium*	*Tin*	*Iron*
Dull olive-yellow.	Yellow-orange.	Brown.	Brownish-black.

A trace of a more sparingly soluble colouring matter is present in the flowers and represents about 1 p.c. of the crude quercetagetin referred to above. It crystallises from alcohol in somewhat indefinite groups of minute needles and dissolves in alkaline solutions with an orange colour passing to green on dilution with water. Though similar in appearance to rhamnetin (quercetin monomethyl ether) it does not contain a methoxy group.

Dyeing properties of the flowers.—Employing mordanted woollen cloth, the following shades are produced:—

Chromium	*Aluminium*	*Tin*	*Iron*
Yellowish-brown.	Pale dull yellow.	Deep yellow-orange.	Brownish-black.

These possess a somewhat redder character than those given by quercitron bark, and are similar to, though not so red as those from patent bark. As quercetagetin mainly occurs in the flowers as glucoside, their tinctorial effect is evidently due to this latter.

QUERCETIN *v.* HORSECHESTNUT and QUERCITRON BARK.

QUERCIMETRIN *v.* GLUCOSIDES.

QUERCIN ; QUERCEMIC ACID *v.* TANNINS.

QUERCITE *v.* INOSITE.

QUERCITRIN *v.* GLUCOSIDES.

QUERCITRON BARK. This important yellow dyestuff, the latest addition to the somewhat meagre list of commercial natural colouring matters, was discovered and introduced by

Bancroft in 1775. In his Philosophy of Permanent Colours he states (II, 113), 'Quercitron bark is one of the objects of a discovery of which the use and application for dyeing are exclusively vested in me, for a term of years by an Act of Parliament in the twenty-fifth year of his present Majesty's reign.'

Quercitron bark is the inner bark of a species of oak known as *Quercus discolor* (Ait.) [*Q. tinctoria*], which is a native of the Middle and Southern States of America. The tree in the south is described as being from 60 to 80 ft. high, with a trunk from 6 to 10 ft. in diameter; but in the north it does not attain to this size. In order to obtain the dyestuff the epidermis or exterior blackish coat of bark is usually removed by shaving and the inner portion then detached and ground. The product may be separated into stringy fibres and a light fine powder, the latter of which contains the principal portion of the colouring matter.

Quercitron bark and its preparations are still used to a considerable extent, although not so much as was formerly the case. This is not only due to the introduction of the artificial colouring matters, but because it has been supplanted for many purposes by the less costly Old Fustic.

Quercetin $C_{15}H_{10}O_7$, the colouring matter of quercitron bark, has been the subject of numerous researches, and many of these unfortunately resulted in the publication of complicated and unsatisfactory formulæ. At an early stage it was ascertained that quercetin does not exist in the plant, at least to any extent in the free condition, but in the form of its glucoside *quercitrin*.

To prepare quercetin the following method devised by the late Sir W. H. Perkin, and employed by him for several years on the manufacturing scale, gives good results. Quercitron bark dust is macerated with moderately strong salt solution to remove gummy substances, filtered, and then extracted with dilute ammonia. The cold ammoniacal liquid is treated with a slight excess of hydrochloric acid, causing the separation of certain impurities in the form of a brown flocculent precipitate. This is removed, and the pale yellow acid solution of the glucoside is boiled for about 30 minutes. The glucoside is thus hydrolysed and almost chemically pure quercetin separates in the form of pale yellow needles, which are collected while the mixture is still warm and washed with water. It is readily soluble in alcohol, and dissolves in alkaline solutions with a yellow colour. With aqueous lead acetate it gives a bright orange-red precipitate, and with alcoholic ferric chloride a dark green colour.

The most important of the early investigations of quercetin was carried out by Liebermann and Hamburger (Ber. 12, 1178), who assigned to it the formula $C_{24}H_{16}O_{11}$, and to quercitrin the formula $C_{36}H_{38}O_{20}$. Herzig (Monatsh. 5, 72; 6, 863; 9, 537; 12, 172; 14, 53; 15, 697), who has carried out an elaborate series of researches on this subject, at first adopted this formula. Subsequently it was ascertained that quercetin was in reality $C_{15}H_{10}O_7$, and this received support by the preparation of its compounds with mineral acids by Perkin and Pate (Chem. Soc. Trans. 1895, 67, 647).

When quercetin is fused with alkali, it gives *protocatechuic acid* and *phloroglucinol*, and if its alkaline solution is oxidised with air, the same products are obtained. By the more gentle action of the alkali Hlasiwetz and Pfaundler (J. 1864, 561) obtained certain intermediate products of the hydrolysis, *paradiscetin* $C_{15}H_{10}O_6$, yellow needles, *quercetic acid* $C_{15}H_{10}O_7$, colourless needles, and *quercimeric acid* $C_8H_6O_5,H_2O$, colourless crystals. Herzig and others who have re-investigated this decomposition have been unable to obtain the substances of Hlasiwetz and Pfaundler, and if these compounds are in reality chemical individuals, it seems likely that their formation was due to the action of some special impurity contained in the alkali employed by these chemists.

On acetylation quercetin gives a *pentaacetyl compound* $C_{15}H_5O_7(C_2H_3O)_5$, colourless needles, melting at 191°–195°, but on methylation with methyl iodide the *tetramethyl ether* $C_{15}H_6O_3(OCH_3)_4$, long yellow needles, m.p. 156°–157° (H.), is produced. A free hydroxyl group is still present in this compound, and it yields with alcoholic potash a bright yellow salt decomposable by water, and a *monoacetyl* derivative $C_{15}H_5O_3(C_2H_3O)(OCH_3)_4$, needles, m.p. 167°–169° (H.). The *ethylation* product

$$C_{15}H_6O_3(OC_2H_5)_4$$

yellow needles, m.p. 120°–122°, is similarly constituted, and gives the *acetyl* compound $C_{15}H_5O_3(OC_2H_5)_4(C_2H_3O)$, m.p. 151°–153°.

When heated with alcoholic potash, quercetin tetramethyl ether forms *veratric acid* and a syrupy phloroglucinol derivative (H.), and this latter has been shown (Perkin and Allison, Chem. Soc. Trans. 1902, 81, 471) by means of its disazobenzene derivative to consist of *phloroglucinol monomethyl ether*. Quercetin tetraethyl ether exhibits a similar behaviour.

The following is a list of the more important derivatives of quercetin: *Dibromquercetin* $C_{15}H_8Br_2O_7$, yellow needles, m.p. 233°–235° (H.), *acetyl dibromquercetin* $C_{15}H_3Br_2O_7(C_2H_3O)_5$ (H.), *dibromquercetin tetraethyl ether*, yellow needles, m.p. 169°–173°, *quercetin triphenylcarbamide* $(OH)_2{\cdot}C_{15}H_5O_5(OCO{\cdot}NH{\cdot}C_6H_5)_3$ (Tesmer, Ber. 1885, 18, 2609), *triacetyl quercetin*

$$C_{15}H_7O_7(C_2H_3O)_3$$

colourless needles, m.p. 167°–169°, and *tetraacetyl quercetin* $C_{15}H_6O_7(C_2H_3O)_4$, m.p. 193°–194° (Perkin, Chem. Soc. Trans. 1899, 75, 449), *benzoyl quecertin* $C_{15}H_5O_7{\cdot}(C_7H_5O)_5$, m.p. 239° (Dunstan and Henry, Chem. Soc. Trans. 1898, 73, 219). With mineral acids in the presence of acetic acid, quercetin gives *quercetin sulphate* $C_{15}H_{10}O_7{\cdot}H_2SO_4$, *quercetin hydrobromide*

$$C_{15}H_{10}O_7{\cdot}HBr$$

quercetin hydrochloride $C_{15}H_{10}O_7{\cdot}HCl$, and *quercetin hydriodide* $C_{15}H_{10}O_7{\cdot}HI$, which crystallise in orange needles and are decomposed by cold water (P. and P.). *Monopotassium quercetin* $C_{15}H_9O_7K$ and *monosodium quercetin* $C_{15}H_9O_7Na$, orange needles, are produced by the action of alcoholic potassium and sodium acetates (Perkin, Chem. Soc. Trans. 1899. 75, 438). *Aminoquercetin* $C_{15}H_4O_2(OH)_5NH_2$, pale yellow needles, has been obtained by Watson (Proc. Chem. Soc. 1911, 27, 163) by the action of hydriodic acid (1·7) on aminopentamethylquercetin. The *hydrochloride* $C_{15}H_{11}O_7{\cdot}N{\cdot}H_2HCl$, yellow needles, the *hydriodide*, *sulphate*, and

acetyl derivative, colourless rhombs, m.p. 151°–153°, are also described. Aminoquercetin dyes mordanted wool browner and deeper colours than quercetin itself.

Quercetin is a strong dyestuff, and gives with mordanted wool the following shades, which are almost identical with those produced by fisetin :—

Chromium	*Aluminium*	*Tin*	*Iron*
Red-brown	Brown-orange	Bright orange	Olive-black

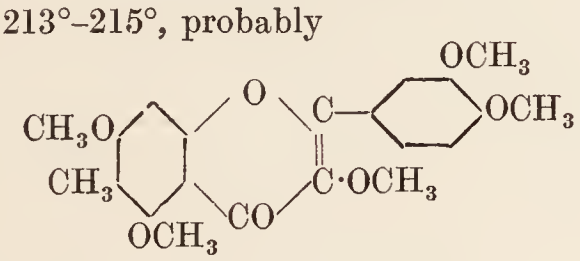
The suggestion that quercetin was probably *hydroxyfisetin* is due in the first place to Herzig, and this has been substantiated by the synthesis of this colouring matter (*see* below).

It has been found (Waliaschko, Arch. Pharm. 1904, 242, 225) that by employing methyl sulphate in the methylation of quercetin, *quercetin pentamethyl ether* $C_{15}H_5O_2(OCH_3)_5$, colourless needles, m.p. 148°, can be produced.

In 1913, however, it was shown by Perkin (Chem. Soc. Trans. 103, 1632) that if a methyl alcoholic solution of quercetin is diluted with an excess of methyl iodide, and boiled with gradual addition of alcoholic potassium hydroxide solution pentamethyl quercetin can be readily prepared. At the same time a small amount of *methyl quercetin pentamethyl ether*

$$CH_3{\cdot}C_{15}H_4O_2(OCH_3)_5$$

m.p. 213°–215°, probably



and *methylquercetin tetramethyl ether*

$$CH_3{\cdot}C_{15}H_5O_3(OCH_3)_4$$

colourless needles, m.p. 184°–185°, the *monacetyl* derivative of which melts at 178°–180°, were produced. Employing ethyl iodide in a similar manner *quercetin pentaethyl ether*, $C_{15}H_5O_2(OEt)_5$, colourless prismatic needles, m.p. 116°–118°, is formed in excellent yield (Chem. Soc. Proc. 1912, 28, 329).

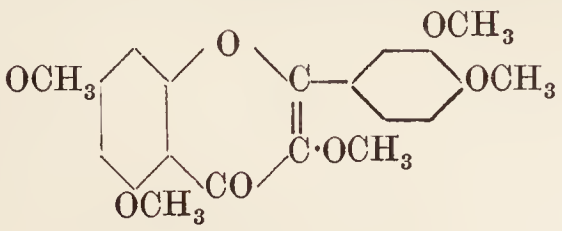
From quercetin pentamethyl ether Watson (Proc. Chem. Soc. 1911, 27, 163) has prepared the following compounds: *Nitropentamethylquercetin* $C_{15}H_4O_2(OCH_3)_5{\cdot}NO_2$, yellow needles, m.p. 202°–204°, *aminopentamethylquercetin*

$$C_{15}H_4O_2(OCH_3)_5{\cdot}NH_2$$

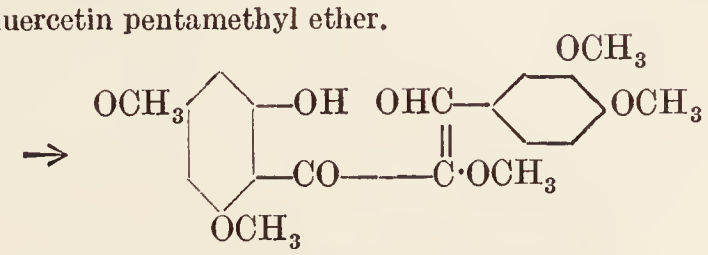
colourless prisms, m.p. 200°–202°, *pentamethylquercetin hydrobromide* $C_{20}H_{20}O_7{\cdot}HBr$, *hydrochloride* $C_{20}H_{20}O_7{\cdot}HCl$, *sulphate* $C_{20}H_{20}O_7{\cdot}H_2SO_4$, *nitrate* $C_{20}H_{20}O_7{\cdot}HNO_3$, yellow needles, *trinitropentamethylquercetin* $C_{15}H_2O_2(OCH_3)_5(NO_2)_3$, m.p. 190°–205°, *dibrompentamethylquercetin* $C_{15}H_3O_2{\cdot}Br_2{\cdot}(OCH_3)_5$, colourless prisms, m.p. 173°–175°, *dibrompentamethylquercetin hydrobromide* $C_{20}H_{18}O_7{\cdot}Br_2{\cdot}HBr$, *dibromnitropentamethylquercetin* $C_{15}H_2O_2Br_2{\cdot}(OCH_3)_5NO_2$, yellow rhombs, m.p. 173°–175°, *pentamethylquercetin diazonium chloride* $C_{15}H_4O_2{\cdot}(OCH_3)_5{\cdot}N_2{\cdot}Cl$, yellow needles, *sulphate* yellow needles, and *pentamethylquercetin-azo-β-naphthol*

$$C_{15}H_4O_2(OCH_3)_5{\cdot}N_2{\cdot}C_{10}H_6OH$$

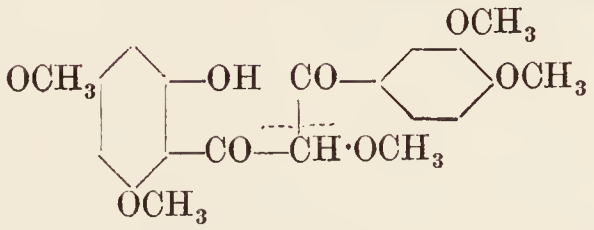
Pentamethylquercetin, when hydrolysed with alcoholic potash (Herzig, Ber. 1909, 42, 155), gives, together with *veratric acid*, the *methoxy derivative of the fisetol dimethyl ether*, which he obtained (Monatsh. 1891, 12, 187) by the hydrolysis of fisetin tetramethyl ether. The reaction may be expressed as follows :—



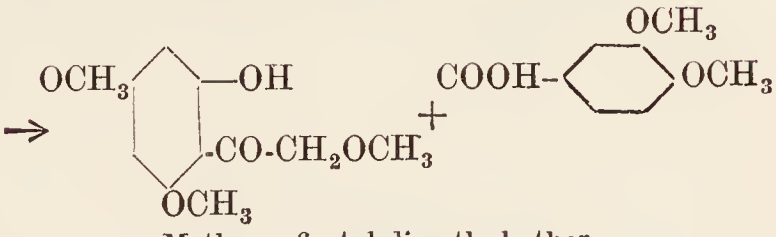
Quercetin pentamethyl ether.



Intermediate compound.

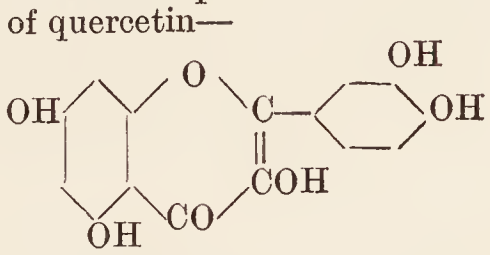


Hydroxy pentamethoxybenzoylacetophenone.

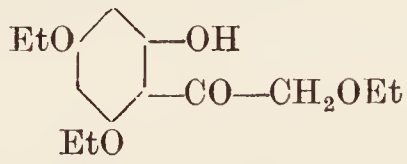


Methoxy fisetol dimethyl ether.

and affords a clear proof of the flavonol constitution of quercetin—



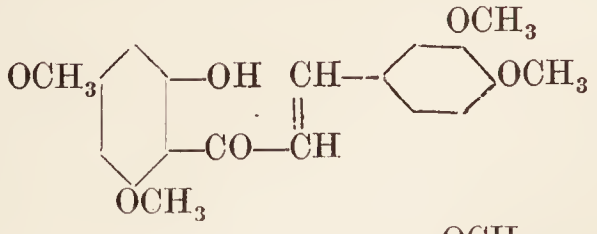
In the same way methyl quercetin pentamethyl ether gives veratric acid and *methoxy methyl fisetol dimethyl ether*, fine needles, m.p. 148°–149°, whereas quercetin pentaethyl ether forms *hydroxy fisetol triethyl ether*—



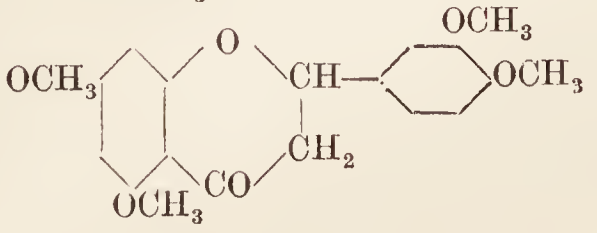
which melts at 96°–97° (Perkin, *l.c.*).

Quercetin has been synthesised by v. Kostanecki, Lampe, and Tambor (Ber. 1904, 37, 1402) by a series of reactions similar to those which had been successfully employed for the preparation of fisetin. The starting-point of the synthesis was 2-hydroxy-4.6.3′.4′-tetramethoxychalkone, and the following formulæ indicate the procedure adopted (compare fisetin) :—

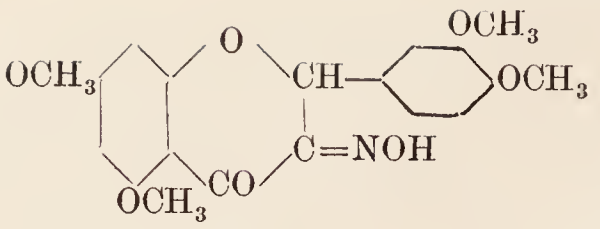
(1)



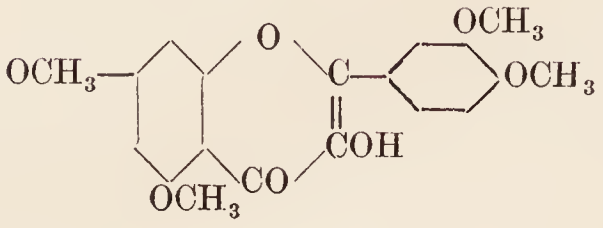
(2)



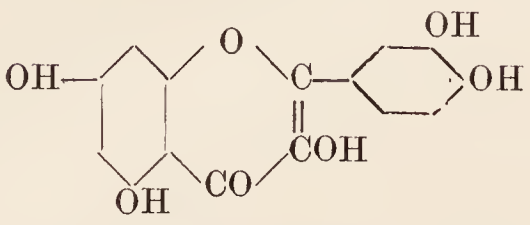
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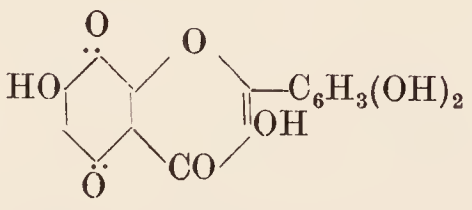
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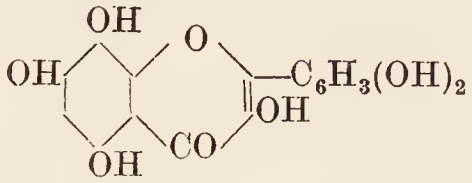
(5)



According to Nierenstein and Wheldale (Ber. 1911, 44, 3487) quercetin by oxidation with chromic acid is converted into *quercetone*, deep red needles (m.p. above 300°) which, like anthrocyanin, dissolves in alkali hydroxides with a blue and in sulphuric acid with a red coloration. It possesses the formula



(compare Kostanecki and Tambor, Ber. 1902, 35, 1869 ; *ibid.* 1906, 39, 4012). When heated with zinc dust and acetic anhydride yields the acetyl derivative (amorphous) of the hydroxyquercetin



This pentahydroxyflavonol, yellow needles, melts at 352°–355°, gives a colourless *hexamethyl derivative*, m.p. 147°–149°. *See* also Nierenstein, Chem. Soc. Trans. 1917, 111, 4.

Quercitrin, the glucoside of quercetin, was first isolated from quercitron bark by Chevreul, and has been examined by numerous chemists. The method usually employed for the preparation of this substance is that devised by Zwenger and Dronke (Ann. Suppl. 1, 267), and this was subsequently utilised by Liebermann and Hamburger (Ber. 12, 1179).

Quercitron bark is extracted with 5–6 times its weight of boiling 50 p.c. alcohol, the extract evaporated to one-half, and treated with a little acetic acid, followed by lead acetate solution. The precipitate is removed, sulphuretted hydrogen is passed through the filtrate, and after removal of lead sulphide the clear liquid is evaporated to dryness. The residue is dissolved in a little hot alcohol, the solution treated with water, and the crude quercitrin which separates on cooling is purified by repeated crystallisation from water.

A very convenient source of quercitrin is *yellow flavine* (Perkin, private communication), which consists almost entirely of this substance, and is usually free from quercetin. A hot aqueous extract of this material gives, on cooling, a crystalline precipitate of the glucoside, and this by recrystallisation from water with the aid of animal charcoal is quickly purified.

Quercitrin crystallises in very pale yellow, almost colourless, leaflets, insoluble in cold water, somewhat readily so in alcohol. Aqueous lead acetate gives a bright yellow precipitate. The generally accepted formula for quercitrin is $C_{21}H_{22}O_{12}\cdot 2H_2O_4$ (Herzig, Monatsh. 14, 53), and its hydrolysis with acids into rhamnose (Hlaziwetz and Pfaunder) and quercetin is usually expressed as follows :—

$$C_{21}H_{22}O_{12}+H_2O=C_{15}H_{10}O_7+C_6H_{14}O_6$$

According to C. W. Moore, however (Proc. Chem. Soc. 1910, 26, 183), the true composition of quercitrin is $C_{21}H_{20}O_{11}\cdot 2H_2O$, and the equation representing its hydrolysis should be as follows :—

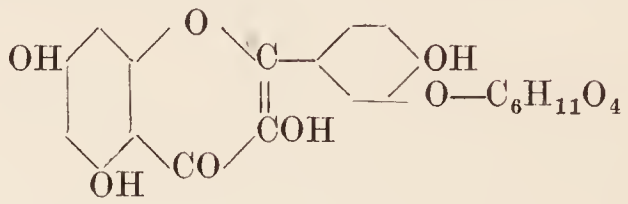
$$C_{21}H_{20}O_{11}+H_2O=C_{15}H_{10}O_7+C_6H_{12}O_5$$

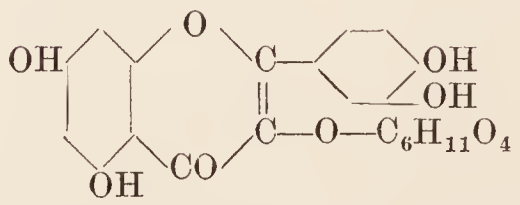
When air-dried quercitrin melts at 182°–185°, and in the anhydrous condition at 250°–252°.

It was formerly considered that the glucosides (colouring principles) were hydrolysed during the dyeing operation, and that the shades thus obtained were due not to the glucosides, but to the free colouring matters. This in certain cases is correct, especially when the plant contains an enzyme capable of effecting the hydrolysis ; but on the other hand, in many cases the glucoside is itself the colouring matter and directly responsible for the dyeing effect. Quercetrin is an instance in point (Perkin, Chem. Soc. Trans. 1902, 81, 479), and gives upon mordanted fabrics shades which are distinct from those of quercetin itself—

	Chromium	*Aluminium*	*Tin*	*Iron*
Quercitrin	Fullbrown-yellow	Full golden yellow	Lemon yellow	Deep olive
Quercetin	Red-brown	Brown-orange	Bright orange	Orange black
Kaempferol	Brown-yellow	Yellow	Lemon yellow	Deep olive brown

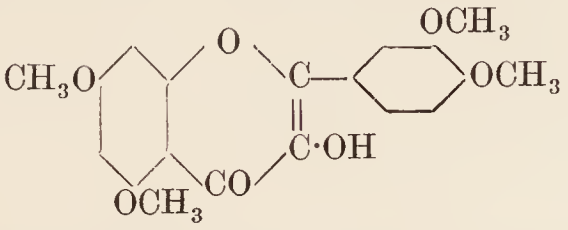
In dyeing property quercitrin very closely resembles kaempferol (*see* GALANGA ROOT), and, indeed, differs but little from morin (old fustic) and luteolin (weld) in this respect. It thus appears probable that the constitution of the glucoside is to be represented by one of the two following formulæ :—





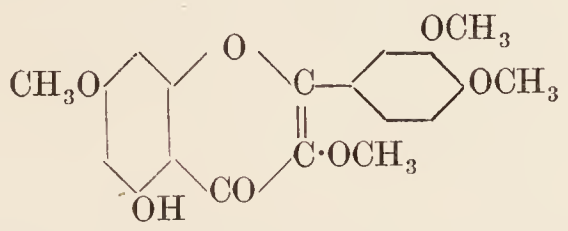
By the action of diazomethane on quercitrin (Herzig and Schönbach, Monatsh. 1912, 33, 673), the free hydroxyl groups of the quercetin nucleus are readily methylated, and subsequently one methyl enters the rhamnose nucleus giving *pentamethylquercitrin*, a light yellow amorphous powder. This when hydrolysed by dilute acid gives colourless *tetramethylquercetin*, $C_{15}H_6O_3(OCH_3)_4$, crystallising in needles, m.p. 195°–198°, the *acetyl compound* of which melts at

160°–163°. Quercetin with diazomethane yields also this colourless tetramethyl compound, in addition to quercetin pentamethyl ether (Herzig and Böttcher, *ibid.* 683). Colourless quercetin tetramethyl ether is idential with the 1 : 3 : 3′ : 4′ tetramethoxyflavonol of v. Kostanecki, Lampe, and Tambor (Ber. 1904, 37, 1402)—



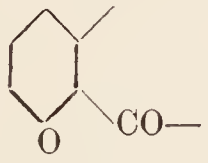
and consequently it is evident that quercitrin may be represented by the second formula given above.

Yellow quercetin tetramethyl ether—



according to these authors, cannot be further methylated with diazomethane, but the immunity of the ortho-hydroxyl to this reagent is only exerted when the other hydroxyls are substituted.

Pfeiffer (Ber. 1911, 48, 1269) has shown, in the case of hydroxy ketones, that the hydroxyl in the ortho-position relatively to the carbonyl group reacts with stannic chloride in benzene solution to form a substitution compound of the type—



$SnCl_3$.

whereas the hydroxyls in other positions give only addition products. According to Herzig and Böttcher yellow and colourless quercetin tetramethyl ethers obey this rule, the former giving a substitution and the latter an addition product.

The colours given by quercitrin possess a somewhat faster character than those derived from quercetin.

Commercial Preparations.

Flavin. This is the most important commercial preparation of quercitron-bark ; it seems to have been first imported to this country from America. The details of its manufacture have been guarded with much secrecy, and analyses of commercial samples show that different methods have been adopted by different makers. Some specimens consist essentially of quercitrin, and are known as *yellow* flavin, while others contain only quercetin, and are known as *red* flavin. The former have probably been prepared by merely extracting the bark with water and high-pressure steam, or, as it is said, with steam only, at a temperature of 102°–103°.

The best qualities of flavin are those in which the colouring matter is present as more or less pure quercitrin, and entirely free from woody fibre. Red flavin is prepared by rapidly extracting the powdery portion of rasped quercitron bark with ammonia or other alkali, and boiling the solution with sulphuric acid. The precipitate thus produced is ultimately collected, washed with cold water till free from acid, and finally dried. Flavin of this character has about sixteen times the tinctorial value of quercitron-bark. It is not very soluble, but it yields with aluminium and especially with tin mordants, much more brilliant colours than does quercitron bark.

Patent bark, or ‘ commercial quercetin,’ is a preparation of quercitron bark analogous to the garancin made from madder. It is manufactured in a similar manner, viz. by boiling, for about 2 hours, 100 parts finely-ground quercitron bark, 300 parts water, and 15 parts concentrated sulphuric acid. The product is collected on a filter, washed free from acid, and dried. The yield is about 85 p.c. of the bark employed, while its colouring power is much greater. It seems to have been first manufactured in 1855 by Leeshing.

Bark-liquor is simply an aqueous extract of quercitron bark, and is sold with a sp.gr. of 1·66°–1·255°.

Application.—Quercitron bark, patent bark, and bark extracts are chiefly employed by the calico and woollen printer. The latter are used in the preparation of steam-yellows, olives, chocolates, &c., in conjunction with aluminium, tin, chromium, and iron mordants. The former were at one time largely employed in conjunction with garancin, for the production of various compound shades, *e.g.* chocolate, dull red, orange, &c. Now they may be used in a similar manner along with alizarin. When used alone, quercitron bark and patent bark give, with aluminium mordant yellow, with tin orange, with chromium olive-yellow, with iron greenish-olive colours.

Flavin is chiefly used in wool dyeing for the production, in single-bath, of bright yellow and orange, fast to milling, or along with cochineal to obtain a bright scarlet. The mordant employed is stannous chloride and oxalic acid or cream of tartar.

On cotton all the quercitron colours are but moderately fast to light ; on wool and silk the chromium, copper, and iron colours are fairly fast, whereas the aluminium and tin colours are only moderately so.

Glucosides of Quercetin.

Rutin was discovered by Weiss (Chem. Zentr. 1842, 305) in the leaves of a rue (*Ruta graveolens* [Linn.]), and was subsequently isolated from capers (*Capparis spinosa* [Linn.]) by Rochleder and Hlasiwetz (Ann. Chem. Pharm. 82, 196), and by Schunck (Manchester Memoirs, 2 Ser. 155, 122, 1858) from buckwheat (*Fagopyrum esculentum* [Moench.]). Whereas Hlasiwetz (Ann. Chem. Pharm. 96, 123) came to the conclusion that rutin was identical with quercitrin, it was shown by Zwenger and Dronke (*ibid.* 123, 145) that this could not be the case, because on hydrolysis rutin gives quercetin and two molecules of sugar. Schunck (Chem. Soc. Trans. 1888, 53, 262 ; 67, 30) showed that the formula of rutin is $C_{27}H_{32}O_{16},2H_2O$, and that on hydrolysis it is converted into *quercetin* and 2 molecules of rhamnose—

$$C_{27}H_{32}O_{16}+3H_2O=C_{15}H_{10}O_7+2C_6H_{11}O_6$$

Rutin, moreover, was identical with the *sophorin*, which Foerster (Ber. 15, 214) had isolated from the *Sophora japonica*.

It has been shown by Schmidt (Chem. Zentr. 1901, ii. 121) that by the hydrolysis of rutin glucose is also produced, the formula of this substance being, therefore, $C_{27}H_{30}O_{16}$—

$$C_{27}H_{30}O_{16}+3H_2O=C_{15}H_{10}O_7+C_6H_{12}O_6+C_6H_{14}O_6$$

Rutin forms pale yellow glistening needles, sparingly soluble in water, and is said to melt above 190°. With alcoholic potassium acetate it gives a bright yellow *monopotassium salt* (Perkin, Chem. Soc. Trans. 1899, 75, 440).

According to Schmidt, *violaquercitrin* (viola-rutin) is identical with rutin (*ibid.* 1908, 246, 274), and Perkin (*ibid.* 1910, 97, 1776) has shown that *osyritin* (*Colpoon compressum* (Berg.) [*Osyris compressa*]) (*ibid.* 1902, 81, 477) and *myrticolorin* (*Eucalyptus macrorhyncha* [F. Muell.]) (Smith, *ibid.* 1898, 73, 697) in reality consist of this substance.

The dyeing properties of rutin are similar to, though weaker than those of quercitron bark. The following shades are given on mordanted woollen cloth :—

Chromium	*Aluminium*	*Tin*	*Iron*
Brown-yellow	Full golden yellow	Lemon yellow	Dull brown

Quercimeritrin, $C_{21}H_{20}O_{12}$, yellow plates, m.p. 247°–249°, almost insoluble in boiling water, is contained in cotton flowers (*Gossypium herbaceum*) (Linn.) (Perkin (*ibid.* 1909, 96, 2183), and in the bark of the *prunus seratina* (Ehrh.) (Finnemore Pharm. Journ. 1910 (iv.) 31, 604). By digestion with boiling dilute sulphuric acid it is hydrolysed according to the equation—

$$C_{21}H_{20}O_{12}+H_2O=C_{15}H_{10}O_7+C_6H_{12}O_6$$

into quercetin and glucose. On mordanted wool it gives the following shades :—

Chromium	*Aluminium*	*Tin*	*Iron*
Reddish brown	Orange yellow	Bright orange	Olive brown

which are very similar to those given by quercetin itself, and indicate that the sugar is attached to the phloroglucinol nucleus of this colouring matter. *Acetyl quercimeritrin*

$$C_{21}H_{12}O_{10}(C_2H_3O)_8$$

needles, melts at 214°–216°. *Isoquercitrin*

$$C_{21}H_{20}O_{12}$$

is also contained in cotton flowers. It consists of yellow needles, m.p. 217°–219°, and when hydrolysed by acid gives quercetin and glucose—

$$C_{21}H_{20}O_{12}+H_2O=C_{15}H_{10}O_7+C_6H_{12}O_6$$

It dyes mordanted wool shades which are entirely distinct from those given by quercimeritrin, but closely resemble those yielded by quercitrin, and in this case the sugar group is not attached to the phloroglucinol nucleus of the quercetin molecule.

Chronium	*Aluminium*	*Tin*	*Iron*
Brownish yellow	Golden yellow	Lemon yellow	Brown olive

Incarnatrin $C_{21}H_{20}O_{12},3H_2O$ is present in the 'carnation or crimson' clover, *Trifolium incarnatum* (Linn.) (Rogerson, *ibid.* 1910, 97, 1008), and forms yellow prismatic needles, m.p. 242°–245°. It is hydrolysed by acid according to the following equation :—

$$C_{21}H_{20}O_{12}+H_2O=C_{15}H_{10}O_7+C_6H_{12}O_6$$

into quercetin and a sugar, the osazone of which melts at 203°–205°. It is not identical with quercimeritrin.

Red clover flowers (*Trifolium pratense* [Linn.]) also contain a glucoside of quercetin, which crystallises in yellow needles, m.p. 235°, but as yet has not been completely examined (Power and Salway, *ibid.* 1910, 97, 244).

Other sources of Quercetin.

Heather (*Calluna vulgaris* [Salisb.]) in former times was used as a dyestuff producing a yellow colour upon woollen goods (Crookes, Dyeing and Calico Printing, 1874, 511). Although now almost superseded, it was until recently employed in the home industries of outlying districts, such as the Highlands of Scotland. It contains *quercetin* (Perkin and Newbury, Chem. Soc. Trans. 1899, 75, 837). According to the late J. J. Hummel, the *Erica tetralix* (bell heather) and the *Erica cinerea* contain only traces of yellow colouring matter. Leuchs (Farben und Färbekunde, 2, 320) refers to the tanning property of heather, and notes that the effect resembles in character that grown by oak bark. According to H. R. Procter it contains 6·4 p.c. of tannin.

White clover (*Trifolium repens* [Linn.]) was at one time employed to a limited extent in country districts for dyeing yellow. A cursory examination of these flowers by Perkin and Phipps (*ibid.* 1904, 85, 58) has indicated the presence of quercetin in the form of glucoside.

Podophyllum Emodi (Wall.) is a small herbaceous plant which grows abundantly in Northern India. The root, or more strictly, the rhizome, has long been used in Indian medical practice, and acts as a powerful purgative. It has been shown by Dunstan and Henry that this rhizome contains *quercetin* in notable amount (*ibid.* 1898, 73, 219), and, according to Hummel (*ibid.*), it compares satisfactorily in dyeing property with quercitron bark. See also articles, Onion Skins, Persian Berries, Sophora Japonica, Cutch (*Acacia catechu* and *Uncaria gambier*), and Sumach (*Osyris compressa*, *Osyris abysinnica*, *Ailanthus glandulosa*, *Rhus rhodanthema*, *Arctostaphylos uva ursi*). Quercetin has also been shown to exist probably as glucoside in tea leaves (Hlasiwetz and Malin, Jahres. 1867, 732); in the flowers of the horse chestnut (Rochleder, *ibid.* 1859, 523); in the bark of the apple tree (Rochleder, *ibid.* 1867, 731); in *Craetagus oxycantha* (may blossom), and yellow wall-flowers. *Chairanthus chieri* (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1568); *Rumex obtusifolius* (seeds), (Perkin, *ibid.* 1897, 71, 1199), *Delphinium zalil* (Asbarg), (Perkin and Pilgrim, *ibid.* 1898, 73, 381), *Prunus spinosa* (flowers), (Perkin and Phipps, *ibid.* 1904, 85, 56), and *Thespasia lampas* (P. *ibid.* 1900, 95, 1859); the flowers of *Poinciana regia* (Bengal); *Woodfordia floribunda* and the common fuschia (*F. Macrostema globosa*), Perkin and Shulman, Chem. Soc. Proc. 1914, 30, 177. A. G. P.

QUERCYITE *v.* Phosphorite.

QUICKSILVER *v.* Mercury.

QUIETOL. Trade name for dimethylaminodimethyl *iso* valerylpropyl ester hydrobromide.

QUILLAIA BARK. Official quillaia bark is the inner part of the bark of *Quillaia Saponaria*, Molina, and its main use depends upon the relatively large quantity of saponin it contains to which is due its property, when in solution, of lowering the interfacial tension between substances leading to its employment as a foaming, emulsifying, or cleansing agent. Other forms of quillaia bark are met with in commerce, viz. quilled quillaia bark (*Q. Smegmadermos* D.C.) and the Flat, False Barks (*Q. Peppigi* Walpers or *Q. Lancifolia* Don), which appear to be only different forms of *Q. Saponaria*. The usual organic solvents extract only very small amounts of matter from the various barks; water dissolves nearly a third of the weight of the bark consisting of saponin, sugars, gum, &c. For methods of estimating the saponins, *see* Kobert, Abderhaldens Biochem. Handlexicon, 7, 165 *et seq.* According to Cofman-Nicoresti and Tallantyre (Pharm. J. 105, 1920, 94), the most convenient process is to boil the clarified aqueous extract with dilute hydrochloric acid, and dry and weigh the precipitated sapogenin:

$$2C_{19}H_{30}O_{10}+8H_2O=4C_6H_{12}O_6+C_{14}H_{28}O_4$$
Quillaiac acid — Glucose — Quillaiac Sapogenin.

$$2C_{17}H_{26}O_{16}+7H_2O=4C_6H_{12}O_6+C_{10}H_{18}O_3$$
Sapotoxin — Glucose — Sapotoxin Sapogenin.

The saponins from quillaia bark, when pure, yield on the average 31·1 per cent. of sapogenin, so that one part of sapogenin is equivalent to 3·22 parts of saponin. According to Koberr (*l.c.*) quillaiac acid yields 33·3 p.c. and sapotoxin 30·0 p.c. of the same sapogenin, the saponins of quillaia bark consisting of one-third quillaiac acid and two-thirds of sapotoxin (*cf.* Hoffman, Kenntniss d. Saponin Substanzen, Stuttgart, 1904; Kruskel, Arbeiten-d. pharmak. *Inst. Zu Dorpat*, 6, 38). Genuine quillaia bark contains upwards of 10 p.c. of saponin, the other varieties slightly less. The official tincture of quillaia consists mainly of an alcoholic solution of saponin.

QUILLAIA SAPOTOXIN *v.* Glucosides.

QUILLAIC ACID *v.* Glucosides.

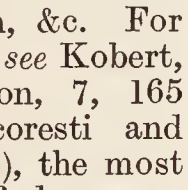
QUINAFORM. Trade name for quinine formate; also for a condensation product of cinchotannic acid and formaldehyde.

QUINALDINE *v.* Quinoline.

QUINAPHENIN. Phenelidine quinine carbonic ester, $Co<^{NH\cdot C_6H_4\cdot OC_2H_5}_{O—C_{20}H_{23}N_2O}$

QUINAPHTHOL. Trade name for quinine β-naphtholsulphonate.

QUINAZOLINE, *pheno*-m-*diazine*,



Prepared by treating a strongly cooled alcoholic solution of *o*-formylaminobenzylamine with zinc and dilute hydrochloric acid, precipitating the zinc chloride double salt, converting this into the chromate and decomposing with 33 p.c. aqueous potassium hydroxide. The 3 : 4-dihydroquinazoline thus formed is oxidised to quinazoline by treatment with potassium ferricyanide in alkaline solution (Gabriel, Ber. 1903, 36, 807; *v.* also Bischler and Lang, Ber. 1895, 28, 292). It forms yellow crystals having a smell like that of naphthalene; m.p. 48°–48·5°; b.p. 243°/772·5 mm. The alkylquinazolinium salts with methyl and ethyl halides, prepared by the usual methods for producing quaternary salts, are stated to greatly lower the blood pressure (Gabriel and Colman, D. R. P. 161401, J. Soc. Chem. Ind. 1905, 1031).

QUINCE GUM *v.* Gums.

QUINCONAL. Quinine diethyl barbiturate.

QUININE LYGOSINATE. Syn. for dihydroxy dibenzalacetone-quinine.

QUINIZARIN. 1 : 4-*Dioxanthraquinone* *v.* Alizarin and allied colouring matters.

QUINIZARIN BLUE, GREEN *v.* Alizarin and allied colouring matters.

QUINOL *v. Hydroquinone*, art. Phenol and its homologues.

QUINONOID THEORY *v.* Colour and Chemical Constitution.

QUINOLCARBOXYLIC ACID *v.* Protocatechuic acid.

QUINOLINE. *Leucoline* C_9H_7N.

History.—Quinoline, in an impure form ('leukol'), was isolated first from coal-tar oil of high boiling point by Runge (Pogg. Annalen, 1834, 31, 68). Subsequently, by distilling quinine, cinchonine, or strychnine with caustic potash Gerhardt obtained a basic oil, 'chinolein' (Annalen, 1842, 42, 310; 44, 279), which was shown by Hofmann to be identical with Runge's base (Annalen, 1843, 47, 76; 1845, 53, 427; *cf.* Hoogewerff and van Dorp, Rec. trav. chim. 1882, 1, 1). The product from either source is not a pure substance, but a mixture of quinoline with some of its homologues (*cf.* Greville Williams, Chem. Soc. Journ. 1872, 25, 658; Jacobsen and Reimer, Ber. 1883, 16, 1084; Krakau, Ber. 1885, 18, 1934), coal-tar quinoline (b.p. 230°–240°) containing 20–25 p.c. of quinaldine (*cf.* Jacobsen, D. R.-P. 23967), and, in addition, a noteworthy quantity of *iso*quinoline (Aktienges., D. R.-P. 40420; Hoogewerff and van Dorp, Rec. trav. chim. 1885, 4, 125). Quinoline and its homologues also occur in brown coal tar (Doebner, Ber. 1895, 28, 106).

Formation.—The pure base has been obtained by distilling cinchonic acid with lime (Koenigs, Ber. 1879, 12, 98), or cinchonine with a mixture of caustic potash and copper oxide (Wyschnegradsky, Ber. 1880, 13, 2318). Synthetically, it can be prepared by the condensation of *o*-aminocinnamic aldehyde (Baeyer and Drewsen, Ber. 1883, 16, 2207), of *o*-aminobenzaldehyde with acetaldehyde (Friedländer and Göhring, *ibid.* 1835), or of *o*-toluidine with glyoxal (Kulisch, Monatsh. 1894, 15, 277); by passing the vapour of 2-methylindole through a red-hot tube (Pictet, Ber. 1905, 38, 1949), or allylaniline over heated lead oxide (Koenigs, Ber. 1879, 12, 453); by dry distillation of acroleïnaniline (Koenigs, Ber. 1880, 13, 911); or, in about 60 p.c. yield, by heating a mixture of aniline, glycerol and sulphuric acid with oxidising agents such as nitrobenzene (Skraup, Monatsh. 1880, 1, 317; *cf.* Blaise and Maire, Bull. Soc. chim. 1908, [iv.] 3, 671).

Preparation.—A mixture of aniline (19 pts.), glycerol (60 pts.) and sulphuric acid (50 pts.), heated by a steam coil to diminish its viscosity, is added slowly to boiling nitrobenzene (12 pts.) in a reflux apparatus, the whole boiled for about 2 hours to complete the reaction, and any unchanged nitrobenzene removed by a current

of air. From the product, rendered alkaline with caustic soda, crude quinoline is obtained by distillation with steam and may be freed from the greater part of the unchanged aniline by fractionation. Further purification is effected by oxidation with dichromate mixture, or by treatment with nitrite and acid, followed by distillation from alkaline solution with steam (Skraup, Monatsh. 1881, 2, 141; Walter, J. pr. Chem. 1894, [ii.] 49, 549). Or, this mixture of aniline, glycerol and sulphuric acid may be boiled with arsenic acid (29 pts.) in an open dish for 2–3 hours (Kneuppel, Ber. 1896, 29, 704; D. R.-P. 87334), or with aniline stannichloride (Druce, Chem. News, 1918, 117, 346; 1919, 119, 271); or with ferric oxide (Barnett, Chem. News, 1920, 121, 205), and the product freed from aniline as just described.

Properties.—Quinoline is a colourless oily liquid, m.p. −19·5° (Altschul and Schneider, Z. physikal. Chem. 1895, 16, 24); b.p. 237·1° under 746·8 mm. (Skraup, *l.c.*), 238° under 760 mm. (Kahlbaum; for vapour pressure at each degree between 180° and 240°, *cf.* Young, Chem. Soc. Trans. 1889, 55, 485); sp.gr. 1·1063 at 4°/4°, 1·1018 at 10°/10°, 1·0985 at 15°/15°, 1·0955 at 20°/20° (Perkin, Chem. Soc. Trans. 1896, 69, 1214). It has a disagreeable penetrating odour, a bitter acrid taste, and is very hygroscopic, being converted on exposure to moist air into the *hydrate* $C_9H_7N+1\frac{1}{2}H_2O$ (Hoogewerff and van Dorp, Rec. trav. chim. 1882, 1, 9), but is only sparingly soluble in water, although dissolved readily by the ordinary organic solvents. It dissolves certain metallic chlorides, bromides and iodides (Walden, Z. physikal. Chem. 1906, 54, 181), and is soluble in cold alkali bisulphite solutions forming crystallisable compounds which regenerate the base at 60°–70° (Brunck and Graebe, Ber. 1882, 15, 1785).

Reactions.—Quinoline is oxidised only with difficulty by chromic acid mixture (*cf.*, however, de Coninck, Compt. rend. 1899, 128, 682). By bleaching powder it is converted into 1-*chloro*-2-*quinolone* (1-chlorocarbostyril, *cf.* Einhorn and Lauch, Annalen, 1887, 243, 343) and by permanganate in alkaline solution into *quinolinic* (pyridine-2 : 3-dicarboxylic) *acid*, oxalic acid, ammonia, and carbon dioxide (Hoogewerff and van Dorp, Ber. 1879, 12, 747, 983; Skraup, Monatsh. 1881, 2, 147).

With chlorine, quinoline forms neither additive nor substitution products, but with bromine it gives a *tetrabromide*, decomposing on exposure to the air into the *compound* $B{\cdot}HBr,Br_2$ (Grimaux, Bull. Soc. chim. 1882, [ii] 38, 124), which, when heated, is converted into 3-*bromoquinoline* (Claus and Collischonn, Ber. 1886, 19, 2766). With iodine, the *di-iodide*, m.p. 90°, is obtained (Claus and Istel, Ber. 1882, 15, 824), and with iodine chloride the *chloroiodide* B·ClI, m.p. 159·5° (Pictet and Krafft, Bull. Soc. chim. 1892, [iii] 7, 73; Schering, D. R.-P. 30358; Eng. P. 9252 of 1884).

By nitration, a mixture of the 5- and 8-*nitroquinolines* or, by further nitration, of the 5 : 7- and 6 : 8-*dinitroquinolines* is obtained (*cf.* Dufton, Chem. Soc. Trans. 1892, 61, 782; Kaufmann and Hüssy, Ber. 1908, 41, 1735). Anhydrosulphuric acid converts it into a mixture of the 5- and 8-*monosulphonic acids*, or, at higher temperatures, of two *disulphonic acids*.

On reduction with tin (or zinc) and hydrochloric acid, quinoline is converted into the *tetrahydro-* derivative, the four atoms of hydrogen being taken up by the 'pyridine' ring (Wyschnegradsky, Ber. 1879, 12, 1481; 1880, 13, 2400). Tetrahydroquinoline is also one of the products of electrolytic reduction (Merck, D. R.-P. 90308; 104664; Eng. P. 21471 of 1898). With hydriodic acid and amorphous phosphorus at 230°, *hexahydroquinoline* and *decahydroquinoline* are obtained in addition to other substances (Bamberger and Lengfeld, Ber. 1890, 23, 1138). When it is heated with hydrogen and nickel oxide at 240° under 110 atmos., it gives first *tetrahydro-* and then *decahydro-quinoline* (Ipatiew, Ber. 1908, 41, 992); but when its vapour, mixed with hydrogen, is passed over highly active nickel at 130°–140° *decahydroquinoline* is obtained (Sabatier and Murat, Compt. rend. 1914, 158, 309); and at 260°–280°, the products are 2-*methylindole*, *methyl*-o-*toluidine*, and o-*toluidine* (Padoa and Carughi, Atti Lincei, 1906, [5] 15, ii. 113).

As a tertiary base, quinoline with alkyl iodides forms quaternary ammonium (quinolinium) compounds, which in alkaline solution yield 2-alkylquinolones mixed with tetrahydro-1-alkylquinolines (*v.* p. 550).

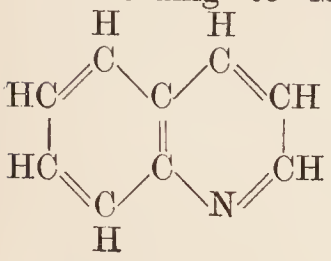
Salts.—As a mono-acid base, quinoline furnishes many salts, but only a few can be mentioned here. The *hydrochloride*, $B{\cdot}HCl+\frac{1}{2}H_2O$, forms deliquescent prisms, m.p. 94°, or, when anhydrous, m.p. 134° (Eckstein, Ber. 1906, 39, 2136); the *chromate*, $B_2{\cdot}H_2Cr_2O_7$, characteristic yellow needles, m.p. 164°–167°, soluble in 275 pts. of water at 10·5° (Hoogewerff and van Dorp, Rec. trav. chim. 1882, 1, 11); the *picrate*, yellow needles, m.p. 203°, from benzene (Goldschmiedt and Schmidt, Monatsh. 1881, 2, 17); the *acid oxalate*, $B{\cdot}C_2H_2O_4$, silky needles; and the *tartrate*, $B_3(C_4H_6O_6)_4$, needles, decomp. 125°, from alcohol (Friese, Ber. 1881, 14, 2805). The *platinichloride*, $B_2{\cdot}H_2PtCl_6+2H_2O$, separates from hot dilute hydrochloric acid in orange-yellow needles, m.p. 218° (Lellmann and Alt, Annalen, 1887, 237, 323; *cf.* Eckstein, *l.c.*), soluble in 1200 pts. of cold water; the *aurichloride*, $B{\cdot}HAuCl_4$, yellow, sparingly soluble needles, m.p. 235°–238°, convertible into the 'abnormal' salt $(B{\cdot}HCl)_2AuCl_3$, m.p. 180° (Fenner and Tafel, Ber. 1899, 32, 3227).

Quinoline combines with many salts of heavy metals, forming, in the case of chlorides, crystalline compounds of the type $B{\cdot}HgCl_2$, $B{\cdot}CdCl_2$, &c., which, by hydrochloric acid, are converted into the corresponding double salts, $(B{\cdot}HCl)_2{\cdot}HgCl_2+2H_2O$, $(B{\cdot}HCl){\cdot}CdCl_2+H_2O$, &c., identical with those formed from quinoline hydrochloride and the metallic chloride (Borsbach, Ber. 1890, 23, 431). For summaries of these 'quinolides' and double salts, also of additive compounds, such as $B{\cdot}Br_2$, $(B{\cdot}HCl){\cdot}Br_2$, &c., which quinoline forms with the halogens, reference should be made to Beilstein's Handbuch. The *chloroiodide*, $C_9H_7N{\cdot}ClI$, was at one time proposed as an iodoform substitute under the name 'quinoiodine' (Schering, D. R.-P. 30358; Eng. P. 9252 of 1884).

Detection.—For the detection of quinoline, the most sensitive reagent (1 in 25,000) is a solution of potassium iodide (7 grms.) and iodine (5 grms.) in water (100 grms.), which gives a

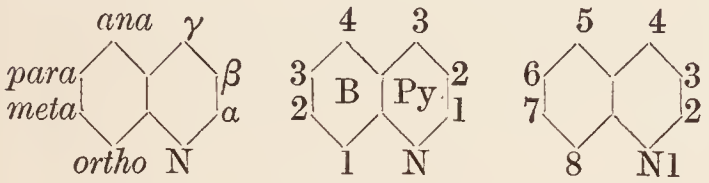
reddish-brown precipitate insoluble in hydrochloric acid; the most characteristic (1 in 3500) is a solution of potassium iodide (5 grms.) and mercuric chloride (1·4 grms.) in water (100 grms.), which produces a yellowish-white precipitate transformed by hydrochloric acid into thin amber-yellow needles (Donath, Ber. 1881, 14, 1771). Less characteristic precipitates are produced by the other alkaloidal reagents.

Constitution of Quinoline.



According to Marckwald (Annalen, 1894, 279, 16), the best available expression for the molecular constitution of quinoline is that suggested by Körner, which represents the molecule as composed of a benzene and a pyridine nucleus having two carbon atoms in common (*cf.* Riedel, Ber. 1883, 16, 1609; Bamberger, Annalen, 1890, 257, 20).

Conventionally, when the object is merely to show the relative position of substituents in the molecule, quinoline is represented by a double hexagon with one side in common. The orientation of substituents is also indicated by the use of distinctive prefixes, letters or numerals,[1] thus—



I. II. III.

System I was introduced by O. Fischer (Ber. 1884, 17, 755, footnote; *cf.* Skraup, Monatsh. 1886, 7, 157); system II by Baeyer (Ber. 1884, 17, 960); and system III, which is now the only one recognised, by the Geneva Congress on Nomenclature in 1892 (Chem. News. 65, 280).

Orientation in the quinoline series is usually determined by oxidation, with the production either of a substituted phthalic acid, or of a substituted pyridine-2 : 3-dicarboxylic acid, the constitution of which is known or can be ascertained (*cf.* Miller, Ber. 1890, 23, 2252; 1891, 24, 1900). If, however, disruption of the ring containing the substituent occurs, a synthetical method may afford the information required. For derivatives containing the substituent in the 'benzene' ring, Skraup's synthetical method is invaluable, as the interpretation of the results is free from ambiguity except in the case of syntheses from *meta*- substituted anilines, which may give rise to both *meta*- and *ana*- derivatives of quinoline. Methods for meeting this difficulty have been devised by Skraup and Brunner (Monatsh. 1886, 7, 139), Tortelli (Gazz. chim. ital. 1886, 16, 336), and Lellmann and Alt (Annalen, 1887, 237, 315).

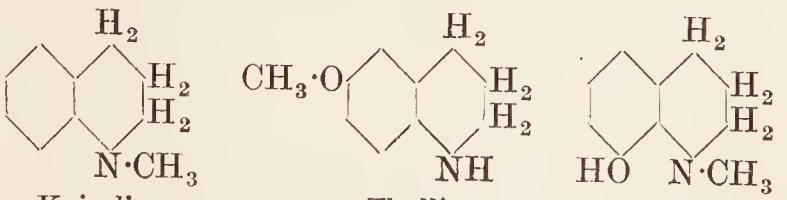
Comparison of the properties of quinoline and naphthalene.—In quinoline, which differs structurally from naphthalene by containing a tervalent nitrogen atom in place of one of the α-methenyl groups, certain of the characteristics of this hydrocarbon are reproduced. Thus, 5-aminoquinoline-4-carboxylic acid yields an internal anhydride (Koenigs and Lossow, Ber. 1899, 32, 717); and lakes are formed by 8-hydroxyquinolines but not by their isomerides (Noelting and Trautmann, Ber. 1890, 23, 3660). But the presence of a nitrogen atom in one of the rings destroys the symmetry of the molecule; consequently the number of mono-substitution derivatives becomes seven instead of only two as in naphthalene. Moreover, reactivity, associated in naphthalene with the α- (1-, 4-, 5-, or 8-) position is restricted in quinoline, as in pyridine, to the 2- and 4- positions (*cf. inter alia*, Koenigs, Ber. 1901, 34, 4326; Ephraim, Ber. 1891, 24, 2818; 1892, 25, 2706; 1893, 26, 2227; Henrich, Ber. 1899, 32, 674), and to these in an approximately equal degree (*cf.* however, Koenigs and Mengel, Ber. 1904, 37, 1323).[1]

The orientating effect of the cyclic nitrogen atom in quinoline resembles closely that of the nitro- group in α-nitronaphthalene. For example, each directs the entering NO_2 or SO_3H group into both the 5- and the 8- position, this being true also not only of quinoline, but of its derivatives so long as strongly 'positive' (*e.g.* OH or NH_2), or strongly 'negative' (*e.g.* NO_2 or SO_3H) radicles, which themselves exercise a directing influence, are absent from the molecule (Decker and Kaufmann, J. pr. Chem. 1911, [ii.] 84, 238; Decker and Remfry, Ber. 1905, 38, 2774).

Uses of Quinoline Derivatives.

Quinoline derivatives, in addition to their limited use in the manufacture of dye-stuffs (*v. Cyanines*, p. 550), have found employment as antipyretics and antiseptics. Quinoline and 6-methoxyquinoline are decomposition products of cinchonine and quinine respectively; investigation of the antipyretic properties of these products showed, however, that the specific action which renders quinine so valuable in cases of malaria is not shared by them (*cf.* Stockmann, J. Physiol. 1894, 15, 245; Führer, Arch. exp. Path. Pharm. 1906, 55, 27); also that 6-methoxyquinoline, which might be expected to excel quinoline in this respect, is the weaker antipyretic of the two (Jaksch, Prager med. Wochensch. 1881, No. 28).

McKendrick and Dewar having shown that reduction (hydrogenation) intensified the physiological effect of bases of the pyridine and quinoline series (Roy. Soc. Proc. 1874, 23, 290), the physiological action of the tetrahydroquinolines was examined, but the results did not fulfil expectation. The best known of these reduction products, kairoline, thalline, and kairine:



Kairoline. Thalline. Kairine.

have marked antipyretic properties—those containing a methyl group in the 1-position being

[1] In the publications of the Chemical Society, the positions, starting with the nitrogen atom, were at one time numbered 1′, 2′, 3′, 4′, those in the other ring being numbered 1, 2, 3, 4.

[1] Susceptibility of the methylquinolines to oxidation by chromic acid does not follow this rule, but diminishes in the order 5, 6, 7, 8, 4, 3, 2, the methyl group in the 5- position being the most and that in the 2- position the least reactive (Miller, Ber. 1890, 23, 2256).

the more valuable (Filehne, quoted, Ber. 1883, 16, 719, 739)—but they all lack the specific properties of quinine.

The relationship of 4-phenylquinoline to *apo*quinenine, and therefore to the cinchona alkaloids (Koenigs and Nef, Ber. 1886, 19, 2427; Koenigs, Ber. 1894, 27, 901; Koenigs and Meimberg, Ber. 1895, 28, 1045), led to the investigation of 6-methoxy- and other derivatives of this base (Koenigs and Jaeglé, Ber. 1895, 28, 1046; Meister, Lucius & Brüning, D. R.-P. 79173, 79871, 80501), but although certain of them are antipyretics, they are useless against malaria, and give rise to dangerous after-effects (*cf.* Mannaberg, Deutsch. Arch. klin. Med. 1897, 59, 185).

Another group of derivatives investigated in this connexion are the quinoline analogues of phenacetin. Analgen (8-ethoxy-5-acetylaminoquinoline) and benzanalgen, the benzoyl-derivative, have antipyretic and antirheumatic properties, which are shared by the 6-ethoxy-derivative, but their insolubility in water and uncertainty in action render them useless in medicine.

Quinoline inhibits putrefaction, but not alcoholic fermentation (Donath, Ber. 1881, 14, 1769). Crurin is the bismuth compound of quinoline thiocyanate, for which antiseptic properties have been claimed (Edinger, D. R.-P. 80768, 86251, 86148; Eng. P. 18516 of 1894). As iodoform substitutes, vioform (iodo-5-chloro-8-hydroxyquinoline), loretin (7-iodo-8-hydroxyquinoline-5-sulphonic acid) and other similar compounds have been proposed, but have found no permanent application in surgery.

The following quinophenol derivatives are disinfectants: 'Quinosol,' prepared by heating 8-hydroxyquinoline in alcoholic solution with potassium pyrosulphate, and 'oxyquinaseptol' (diaphtherin) obtained by heating 8-hydroxyquinoline with phenol and diluted sulphuric acid (Lembach and Schleicher, D. R.-P. 73117; Eng. P. 7803 of 1891; 21968 of 1892).

Halogen Derivatives.

Chloroquinolines are not produced by direct substitution, but can be obtained—

(1) From chloroanilines by Skraup's method. The product from *m*-chloroaniline is a mixture of the 5- and 7-chloroquinolines (La Coste, Ber. 1885, 18, 2941).

(2) From aminoquinolines by the Sandmeyer reaction (*cf.* Wenzel, Monatsh. 1894, 15, 459).

(3) From hydroxyquinolines or quinolones by interaction with phosphorus pentachloride (*cf.* Friedländer and Ostermaier, Ber. 1882, 15, 333; Fischer and Guthmann, J. pr. Chem. 1916, [ii.] 93, 378).

All seven monochloro-, and many di- and tri-chloro-quinolines are known. The mono-derivatives are oils or have a low melting-point; they are less basic than quinoline, the decrease in basicity being most marked in the 2- compound; and they furnish additive compounds with alkyl iodides. The halogen is reactive only in the 2- or 4- position.

Bromoquinolines can be obtained by direct substitution or by suitable modifications of the processes applicable to the chloro- compounds. The seven monobromoquinolines are known, their properties being similar to those of the corresponding chloro- derivatives.

Nitroquinolines.

The mononitration of quinoline is achieved by adding alternately quinoline nitrate and anhydrosulphuric acid of sp.gr. 2·0 to concentrated sulphuric acid (Dufton, Chem. Soc. Trans. 1892, 61, 793; *cf.* Koenigs, Ber. 1879, 12, 449; Claus and Kramer, Ber. 1885, 18, 1243; Noelting and Trautmann, Ber. 1890, 23, 3654). The 5- and 8-nitroquinolines, produced together with some dinitrohydroxyquinoline, can be separated as the 5-isomeride forms a nitrate sparingly soluble in dilute nitric acid (Dufton, *l.c.*), or is converted into a quaternary compound by methyl sulphate (Decker, Ber. 1905, 38, 1154). Further nitration converts the 5-nitro- and 8-nitro- into the 5 : 7- and 6 : 8-dinitro-quinolines respectively; but the 6-nitro- (obtained by Skraup's method) into a mixture of the 5 : 6- and 6 : 8-dinitro-, also the 7-nitro- (obtained by Skraup's method) into a mixture of the 5 : 7- and 7 : 8- dinitro-quinolines (Kaufmann and Decker, Ber. 1906, 39, 3648; Kaufmann and Hüssy, Ber. 1908, 41, 1735).

The nitroquinolines are crystalline; they dissolve in concentrated mineral acids, but their basic properties are feeble, and the salts are mostly decomposed by water. In many cases they form quaternary ammonium compounds with methyl iodide.

Aminoquinolines.

Of the aminoquinolines, six have been described. Those containing the NH_2 group in the 'benzene' ring can be obtained, either by reduction of the corresponding nitro- derivatives with tin and hydrochloric acid, or, like those containing it in the 'pyridine' ring, by heating the corresponding hydroxyquinoline with ammonia-zinc chloride. An aminoquinoline is formed when quinoline dissolved in anhydrosulphuric acid is heated with hydroxylamine sulphate and some ferrous sulphate at 190° (Turski, D. R.-P. 287756).

2-Aminoquinoline is obtained by heating 2-chloroquinoline with ammonium carbonate and ammonia at 210° (Claus and Schaller, J. pr. Chem. 1897, [ii.] 56, 206), and from *o*-aminocinnamonitrile $NH_2 \cdot C_6H_4 \cdot CH : CH \cdot CN$, by interaction with sodium ethoxide (Pschorr, Ber. 1898, 31, 1289). 4-Aminoquinoline can be prepared from cinchonamide by Hofmann's method (Wenzel, Monatsh. 1894, 15, 457). 3-Aminoquinoline has not been described.

The aminoquinolines are crystalline compounds, which act usually as mono- acid bases, give quaternary ammonium compounds with alkyl iodides, and are diazotisable, resembling in this respect primary aromatic amines.

Quinolinesulphonic Acids.

On sulphonation with concentrated sulphuric acid at 220°–230°, quinoline yields the 8-sulphonic acid, but after many hours at 275°–280°, the 6-sulphonic acid (Georgievics, Monatsh. 1887, 8, 577, 639; Badische, D. R.-P. 40901), both the 5- and the 8-sulphonic acids being converted into the 6-sulphonic acid under these

conditions (*ibid.*; Lellmann and Reusch, Ber. 1889, 22, 1391).

The 5- and 8-sulphonic acids are obtained, but in proportions which depend on the temperature and concentration of the acid, when quinoline is heated with anhydrosulphuric acid at 120°–200°; the 8- acid predominates at lower, and the 5- acid at higher temperatures (Bedall and O. Fischer, Ber. 1882, 15, 683, 1979; [1] Riemerschmied, Ber. 1883, 16, 721; La Coste and Valeur, Ber. 1887, 20, 95). According to Claus, a third acid, the 7-sulphonic acid, is also present in the product at 125°–130°, but disappears as the temperature is raised (J. pr. Chem. 1888, [ii.] 37, 261). By further sulphonation with Nordhausen acid at 250°, a mixture of two disulphonic acids is produced (La Coste and Valeur, *l.c.*; La Coste, D. R.-P. 29920).

For the preparation of the 5-sulphonic acid, Skraup's method can be used (Lellmann and Lange, Ber. 1887, 20, 1446), and, by comparison of this acid with the 5-sulphonic acid obtained by sulphonation under different conditions, Lellmann has drawn the conclusion that the latter exists in two forms (*ibid.* 2172; *cf.* Jakubowski, Ber. 1910, 43, 3026).

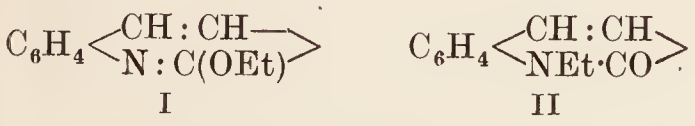
These quinolinesulphonic acids are crystalline, and can be separated from mixtures by fractional crystallisation of the calcium salts. They yield hydroxyquinolines by fusion with caustic alkali; nitriles by distillation with potassium cyanide; and di- or tri-bromoquinolines, with loss of the SO_3H group, on bromination in aqueous solution.

Quinoline-2- and 4-sulphonic acids, obtained by boiling 2- and 4-chloroquinoline respectively with sodium sulphite solution, and the 3-sulphonic acid, which is the most stable of the three, have been described (Besthorn and Geisselbrecht, Ber. 1920, 53, [*B*], 1017).

Hydroxyquinolines.

Six of the seven hydroxyquinolines are known, viz. the 2- and 4- derivatives, and the four quinophenols, containing the OH group in the 'benzene' ring. From each, by combination with alkyl iodides, quaternary ammonium compounds are obtained.

The 2- and 4-hydroxyquinolines are produced either by synthetical methods or from the corresponding chloroquinolines by interaction with water at 120°. They exhibit the properties both of hydroxy- compounds and of ketonic derivatives, forming, for example, two series of ethers—



I

II

are less basic than the quinophenols; and are not reduced by tin and hydrochloric acid, but, in boiling alcoholic solution with sodium, eliminate the OH group forming tetrahydroquinoline. Compounds belonging to type I are classified as hydroxyquinoline derivatives; those of type II are termed *quinolones*, the substance formulated being 1-ethyl-2-quinolone.

The isomeric quinophenols can be prepared from aminophenols by Skraup's reaction; from aminoquinolines by the diazo- reaction; or from quinolinesulphonic acids by fusion with caustic alkali. They resemble the phenols of naphthols in properties, give only one series of ethers on alkylation, yield nitro- derivatives and sulphonic acids, and furnish stable salts with acids or alkalis. The 6- and 8-hydroxyquinolines, moreover, give nitroso- derivatives with nitrous acid, and couple with diazotised bases forming azo- dyes.

(i.) 2-**Hydroxyquinoline** (*carbostyril*) is obtained when ethyl *o*-nitrocinnamate is reduced with alcoholic ammonium sulphide (Friedländer and Ostermaier, Ber. 1881, 14, 1916); when *o*-aminocinnamic acid is boiled for some hours with hydrochloric acid (Tiemann and Oppermann, Ber. 1880, 13, 2070), or 50 p.c. sulphuric acid (Feer and Koenigs, Ber. 1885, 18, 2395); when 2-chloroquinoline is heated with water at 120° (Friedländer and Ostermaier, Ber. 1882, 15, 335); and, in 80 p.c. yield, when acetyl-*o*-aminobenzaldehyde in dilute (10 p.c.) alcoholic solution is boiled with one-third its weight of caustic soda (Camps, Arch. Pharm. 1899, 237, 682). Its occurrence in a sublimate collected from a furnace used for the ignition of residues obtained in sugar manufacture has been noted by Lippmann (Ber. 1905, 38, 3829).

Properties.—It crystallises in prisms, or, from dilute aqueous solution with 1 mol. H_2O in needles, m.p. 199°–200°, is only sparingly soluble in cold water, and insoluble in ammonia, but dissolves in hydrochloric acid or caustic alkali solution. In many of its reactions, it has the properties of a phenol, in others those of a ketone (*cf.* Hartley and Dobbie, Chem. Soc. Trans. 1899, 75, 646); the corresponding ethers are known, *e.g.* the C-*methyl ether*, b.p. 246°–247° (Friedländer and Weinberg, Ber. 1882, 15, 1422), and the N-*methyl ether* (1-methyl-2-quinolone), m.p. 74°, b.p. 324° (Friedländer and Müller, Ber. 1887, 20, 2009). On oxidation with alkaline permanganate, it yields *isatin* and *carbostyrilic* (oxalylanthranilic) *acid* (Friedländer and Ostermaier, Ber. 1882, 15, 332); and on reduction in boiling alcohol with sodium it gives *tetrahydroquinoline* (Knorr and Klotz, Ber. 1886, 19, 3302). For compounds with monosodium salts of polybasic acids, *cf.* Fritzsche, D. R.-P. 283334.

(ii.) 4-**Hydroxyquinoline** (*kynurine*), first obtained from kynurenic acid by sublimation (*cf.* Schmiedeberg and Schultzen, Annalen, 1872, 164, 158), occurs among the oxidation products of cinchonine, cinchonidine, and cinchonic acid (Skraup, Monatsh. 1886, 7, 518; 1888, 9, 801, 818; 1889, 10, 726), and has been synthesised from cinchonamide (Wenzel, Monatsh. 1894, 15, 453), from 4-chloroquinoline by heating it with water at 120° (Skraup, Monatsh. 1889, 10, 726), and from formyl-*o*-aminoacetophenone by boiling it with caustic soda solution (Camps. Ber. 1901, 34, 2709).

Properties.—It forms prisms, m.p. 201°, or, if rapidly separated from solution, needles (with 3 mol. H_2O), dissolves readily in warm water, alcohol or ether, and gives in aqueous solution a carmine coloration with ferric chloride. The *hydrochloride* $B{\cdot}HCl+2H_2O$, and *platinichloride* $B_2{\cdot}H_2PtCl_6+2H_2O$, crystallise in needles. Like carbostyril, it forms both *O*- and *N*- ethers (Wenzel, *l.c.*; Meyer, Monatsh. 1906, 27, 255, 987).

[1] The 'meta'- acid described in these communications is the 5- not the 7- acid.

The 2-carboxylic acid (*kynurenic acid*) occurs in the urine of dogs fed on par-boiled meat (Liebig, Annalen, 1853, 86, 125; 1858, 108, 354; *cf. inter alia*, Kretschy, Monatsh. 1881, 2, 58; Ellinger, Ber. 1904, 37, 1807), and has been synthesised from 4-methoxy-2-methylquinoline (Besthorn, Ber. 1921, 54, [*B*], 1330). It forms prisms, HA+H_2O, melts, when anhydrous, at 288°–289° (Homer, J. biol. Chem. 1914, 17, 509), and is only sparingly soluble in hot water. On oxidation with alkaline permanganate it yields *oxalylanthranilic acid* (Kretschy, Monatsh. 1884, 5, 16).

(iii.) 5-**Hydroxyquinoline**, obtained by fusing quinoline-5-sulphonic acid with caustic alkali (Riemerschmied, Ber. 1883, 16, 721; Lellmann, Ber. 1887, 20, 2174), forms scales, m.p. 224°.

The 8-sulphonic acid is converted, by means of potassium iodide and hypochlorous acid, into the 6-*iodo*-5-*hydroxyquinoline*-8-*sulphonic acid* (Claus, J. pr. Chem. 1896, [ii.] 53, 339; Meister, Lucius & Brüning, D. R.-P. 89600).

(iv.) 6-**Hydroxyquinoline** can be prepared from *p*-aminophenol by Skraup's reaction (Skraup, Monatsh. 1882, 3, 545; D. R.-P. 14976; Eng. P. 678 of 1881); or by fusing quinoline-6-sulphonic acid with caustic alkali (Fischer and Willmack, Ber. 1884, 17, 440; Happ, *ibid.* 191; Meister, Lucius & Brüning, D. R.-P. 26430). It forms prisms, m.p. 193°, which dissolve only very sparingly in cold water.

Reactions.—With nitrous acid, it gives the 5-*nitroso*- derivative (the 5-oxime of quinoline-5 : 6-quinone), convertible by hydroxylamine into the 5 : 6-*dioxime* which forms lakes with mordants (*cf.* Mathëus, Ber. 1888, 21, 1886; Kostanecki and Reicher, Ber. 1891, 24, 158). Diazotised bases couple with it forming *azo*- dyes (Mathëus, Ber. 1888, 21, 1642).

Its potassium salt, heated with carbon dioxide under pressure at 170°, yields *potassium* 6-*hydroxyquinolinecarboxylate* (Schmitt and Altschul, Ber. 1887, 20, 2695).

The methoxy- derivative (6-*quinanisole*), obtained either by the Skraup reaction (Skraup, Monatsh. 1885, 6, 762; Badische, D. R.-P. 28324), or by methylating 6-hydroxyquinoline (Skraup, Monatsh. 1882, 3, 544), is an oil, b.p. 304°–305° (slight decomp.) under 740 mm., sp.gr. 1·1542 at 20°. Its salts, like those of quinine, show blue fluorescence in aqueous solution, and with chlorine water and ammonia give a green coloration. On reduction with tin and hydrochloric acid it furnishes *thalline* (Badische, D. R.-P. 30426).

For 5-iodo-6-hydroxyquinoline, *see* Claus, D. R.-P. 78880.

6-Ethoxyquinoline, b.p. 290°–292°, on nitration, gives the 5-*nitro*- derivative, needles, m.p. 111°. This, when reduced, yields the 5-*amino*- derivative, needles, m.p. (anhydrous) 115°–116°, which forms an *acetyl* derivative, scales, m.p. 163°, and a *benzoyl* derivative, m.p. 144° (Vis, J. pr. Chem. 1893, [ii.] 48, 29; Dahl, D. R.-P. 69035).

(v.) 7-**Hydroxyquinoline**, obtained either from *m*-aminophenol by the Skraup reaction (Skraup, Monatsh. 1882, 3, 559), or by fusing quinoline-7-sulphonic acid with caustic alkali (Fischer, Ber. 1882, 15, 1979), crystallises in prisms, m.p. 235°–238°, is less soluble than the 6-isomeride in water, and in solution shows green fluorescence.

(vi.) 8-**Hydroxyquinoline** (*quinophenol*) is prepared either from *o*-aminophenol by the Skraup reaction (Skraup, Monatsh. 1882, 3, 536; D. R.-P. 14976; Eng. P. 678 of 1881), or from quinoline-8-sulphonic acid by fusion with caustic alkali (Bedall and Fischer, Ber. 1881, 14, 443, 1366). It forms prismatic needles, m.p. 76°, b.p. 266·6° (corr.) under 752 mm. (Skraup, *l.c.*), dissolves only very sparingly in cold water, but readily in alcohol, and, unlike its isomerides, is volatile with steam. The aqueous solutions of its acid or alkali salts are yellow. Esters formed by interaction with salicylyl chloride and acetylsalicylyl chloride have been described (Wolffenstein, D. R.-P. 281007; Eng. P. 16585 of 1914).

Reactions.—By methylation, it is converted into the 8-*quinanisole*, an oil, b.p. 265°–268° (Bedall and Fischer, *l.c.*). With nitrous acid, it furnishes the 5-*nitroso*- derivative (the 5-oxime of quinoline-5 : 8-quinone), convertible by hydroxylamine into the 5 : 8-*dioxime* which forms lakes with mordants (Lippmann and Fleissner, Monatsh. 1889, 10, 794; Kostanecki, Ber. 1891, 24, 151), and with diazotised bases it couples forming *azo*- dyes (Mathëus, Ber. 1888, 21, 1644).

When its sodium salt is heated with carbon dioxide at 140°–150° under pressure, *sodium* 8-*hydroxyquinolinecarboxylate* is obtained (Schmitt and Engelmann, Ber. 1887, 20, 1217, 2690; *cf.* Heyden, D. R.-P. 39662; Eng. P. 10280 of 1886). By interaction with ω-bromacetophenone in presence of alcoholic caustic alkali solution, it yields *acetophenone*-8-*hydroxyquinoline* (Zimmer, D. R.-P. 92755).

Iodochloro-8-hydroxyquinoline (Basler chem. Fab. D. R.-P. 117767; Eng. P. 3915 of 1900); 5 : 6-diiodo-8-hydroxyquinoline (Claus, D. R.-P. 78880); 7-iodo-8-hydroxyquinoline-5-sulphonic acid (Claus, D. R.-P. 72942; Griese, D. R.-P. 190956; Eng. P. 9656 of 1905) and similar compounds (*cf.* Claus, D. R.-P. 73145; Meister, Lucius & Brüning, D. R.-P. 84063) have been proposed as iodoform substitutes. For compounds containing iodine and bismuth, *cf.* Bayer, D. R.-P. 282455; 283825.

8-Ethoxyquinoline, obtained by heating 8-hydroxyquinoline with ethyl bromide and alcoholic caustic soda (Fischer and Renouf, Ber. 1884, 17, 759; Vis, J. pr. Chem. 1892, [ii.] 45, 531), needles, b.p. 285°–287°, forms 5-*nitro*-8-*ethoxyquinoline*, m.p. 128°, on nitration with nitric acid of sp.gr. 1·52. From the corresponding 5-*amino*- derivative, scales, m.p. 114°, an *acetyl* derivative, analgen (the phenacetin of the quinoline series), needles, m.p. 155°, and a *benzoyl* derivative, benzanalgen, a crystalline powder, m.p. 206°, have been obtained (Vis, *l.c.*; D. R.-P. 60308; Dahl, D. R.-P. 65102; 65111; Eng. P. 17493 of 1891; 3147 of 1892). The corresponding *acetyl*-5-*amino*-8-*methoxyquinoline* forms needles, m.p. 178°–179° (Vis, J. pr. Chem. 1893, [ii.] 48, 24; Dahl, D. R.-P. 65110).

8-Hydroxyquinoline-5-sulphonic acid, prepared by sulphonating 8-hydroxyquinoline with cooled anhydrosulphuric acid (Claus and Posselt, J. pr. Chem. 1890, [ii.] 41, 33) has been used as an antiseptic under the name quinosol

(Fritzsche, D. R.-P. 88520; 187869; 187943; Eng. P. 1409 of 1896; 11725 of 1906). For its physiological action, *cf.* Brahms, Z. physiol. Chem. 1899, 28, 439.

2:4-**Dihydroxyquinoline** (*γ-hydroxycarbostyril*) is the only dihydroxy- compound which can be mentioned here. It is obtained by fusing 4-chlorocarbostyril with caustic potash at 200° (Friedländer and Weinberg, Ber. 1882, 15, 2683); by boiling a solution of ethyl acetylanthranilate in dry toluene with sodium (Camps, Arch. Pharm. 1899, 237, 690; Meister, Lucius & Brüning, D. R.-P. 102894); by fusing potassium acetylanthranilate with caustic potash at 250° (Badische, D. R.-P. 117167); by hydrolysing ethyl *o*-aminobenzoylacetate with very dilute hydrochloric acid (Erdmann, Ber. 1899, 32, 3570); or by heating *o*-nitrophenylpropiolic acid with sulphuric acid at 145° (Baeyer and Bloem, Ber. 1882, 15, 2151).

Properties.—It crystallises in needles, does not melt even at 320°, can be sublimed, and is insoluble in ordinary solvents, but dissolves in acids or alkalis. By nitrous acid it is converted into the 3-iso*nitroso*- derivative (*quinisatoxime*), orange-yellow prisms, m.p. 208° (decomp.), which, when boiled with hydrochloric acid, yields isatin and hydroxylamine (Baeyer and Homolka, Ber. 1883, 16, 2216).

2:4-Dihydroxy-3:4-dihydroquinoline, obtained by reduction of *o*-nitrophenyl-*β*-lactic acid with ferrous sulphate (Einhorn, Ber. 1884, 17, 2011; D. R.-P. 28900), needles (with 2 mol. H_2O), m.p. 95°–97°, or (anhyd.) 149°, gives *carbostyril* when boiled with acidified water, or fused. Its 6-methoxy- derivative, needles, m.p. 177°, synthesised from the corresponding *β*-lactic acid, was introduced as an antipyretic (Einhorn, D. R.-P. 55119).

Alkyl Derivatives.

All the seven isomeric methylquinolines are known. Those containing the alkyl radicle in the 'benzene' nucleus have been called toluquinolines, the others methylquinolines. In their general properties the alkyl derivatives resemble quinoline; they are mono- acid bases, form double salts with halogen salts of heavy metals, and with alkyl iodides give quaternary ammonium compounds. The 2- and 4-methylquinolines alone call for detailed mention here.

(i.) **Quinaldine** (2-*methylquinoline*) occurs in coal-tar quinoline to the extent of about 25 p.c. (Jacobsen and Reimer, Ber. 1883, 16, 1084; Jacobsen, D. R.-P. 23967). It is obtained synthetically by warming a mixture of aniline and aldol with concentrated hydrochloric acid (Doebner and Miller, Ber. 1883, 16, 2465); by heating crotonic aldehyde with aniline, nitrobenzene and sulphuric acid (Skraup, Ber. 1882, 15, 897), or lactic acid with aniline and zinc chloride (Wallach and Wüsten, Ber. 1883, 16, 2007; *cf.* Pictet and Duparc, Ber. 1887, 20, 3417), or ethylacetanilide with zinc chloride at 250° (Pictet and Bunzl, Ber. 1889, 22, 1848); by warming *o*-aminobenzaldehyde and acetone in aqueous solution with a small quantity of caustic soda (Friedländer and Göhring, Ber. 1883, 16, 1835); by heating acetonylquinoline with concentrated hydrochloric acid at 170° (Fischer and Kuzel, *ibid.* 165); or by reducing *o*-nitrobenzylideneacetone with stannous chloride and hydrochloric acid (Drewsen, *ibid.* 1954; Meister, Lucius & Brüning, D. R.-P. 22138; Eng. P. 3541 of 1882).

Preparation.—Acetaldehyde (24 kilos.) is added gradually in the course of about six hours to a solution of aniline hydrochloride (30 kilos.) in water (40–50 litres) at a temperature not exceeding 25°, and the mixture stirred at this temperature during two to three days until a sample tested with caustic soda solution gives no separation of oil. Then zinc chloride solution of sp.gr. 1·5 (40 kilos.) is added; the whole evaporated to complete dryness, fused at 275°, mixed with water (150 litres), rendered strongly alkaline by caustic soda solution, and the crude quinaldine, thus separated, purified by fractional distillation, preferably in a vacuum (*cf.* Doebner and Miller, *l.c.*; Ber. 1884, 17, 1699; Schultz, Ber. 1883, 16, 2600; Schering, D. R.-P. 24317; Eng. P. 956 of 1883; Aktienges., D. R.-P. 28217; Eng. P. 4207 of 1883; Mills, Harris and Lambourne, Chem. Soc. Trans. 1921, 119, 1297 [1]).

Properties.—It is a colourless, strongly refractive oil, of slight quinoline-like odour, b.p. 238°–239° under 716 mm. (Doebner and Miller, Ber. 1881, 14, 2814); at 244°–245° under 750 mm. (Hoogewerff and van Dorp, Rec. trav. chim. 1884, 3, 344). The salts, as a rule, are readily soluble, but the *chromate*, yellowish-red needles, is only sparingly soluble in cold water (Doebner and Miller, Ber. 1882, 15, 3075). The *platinichloride* forms prisms, m.p. 228°–229°, and the *picrate*, sparingly soluble needles, m.p. 191° (Pictet and Bunzl, *l.c.*).

Reactions.—By oxidation with concentrated nitric acid, quinaldine is converted into a *nitroquinoline-2-carboxylic acid* (Doebner and Miller, Ber. 1882, 15, 3076); with potassium permanganate it forms *acetylanthranilic acid* and oxalic acid (*ibid.* 3077), and with chromium trioxide and sulphuric acid it yields *quinaldic* (quinoline-2-carboxylic) *acid* (Doebner and Miller, Ber. 1883, 16, 2472). Reduced with tin and hydrochloric acid it gives the *tetrahydro*-derivative (*ibid.* 2467).

When nitrated, preferably below 4°, excess of nitric acid being avoided, it furnishes a mixture of the 5-*nitro*- and 8-*nitro-quinaldines*, the former being the chief product (Decker and Remfrey, Ber. 1905, 38, 2776; *cf.* Doebner and Miller, Ber. 1884, 17, 1699; Gerdeissen, Ber. 1889, 22, 245). Sulphonation with anhydrosulphuric acid at 100° converts it into a mixture of the 6-, meta-,[2] and 8-*mono-sulphonic acids*, of which the '*meta*-' acid constitutes nearly two-thirds and the 8-sulphonic acid nearly one-third (Doebner and Miller, Ber. 1884, 17, 1703; Schering, *l.c.*; D. R.-P. 29819).

Owing to the reactivity of the 2-methyl group, it yields condensation products with

[1] Mills, Harris and Lambourne, who have reinvestigated the Doebner-Miller synthesis, and omit the fusion at 275°, find that ethylaniline, *n*-butylaniline and 6-ethylquinaldine are also products of the reaction, little, if any, tetrahydroquinaldine being formed (*l.c.*).

[2] The evidence that Doebner and Miller's quinaldine-*β*-sulphonic acid is the 5- and not the 7- derivative rests on Rist's production of a quinaldinecarboxylic acid, m.p. 284°, from '*meta*'-nitroquinaldine (Ber. 1890, 23, 3485; *cf.* Richard, *ibid.* 3490), now known to be the 5- and not the 7- derivative (Decker and Remfry, *supra*).

aldehydes, thus resembling 2-methylpyridine (α-picoline). From the product with chloral, *α-quinolineacrylic acid* and *quinoline-2-aldehyde* have been prepared (Miller and Spady, Ber. 1886, 19, 130; Meister, Lucius & Brüning, D. R.-P. 36964). When heated with phthalic anhydride and zinc chloride it is converted into *quinophthalone* (Jacobsen and Reimer, Ber. 1883, 16, 1082; *v.* p. 553).

(ii.) **Lepidine** (4-*methylquinoline*, *iridoline*) occurs in the product formed by distilling cinchonine with caustic potash (Greville Williams, Trans. R. S. Edin. 1856, 21, iii. 377), and is isolated from the fraction, b.p. 250°–260°, by dissolving it in 3–4 parts of warm alcohol, adding 2 parts of sulphuric acid of sp.gr. 1·53, and decomposing by potash the crystalline acid sulphate which separates (Hoogewerff and van Dorp, Rec. trav. chim. 1883, 2, 1). Synthetically it has been prepared by saturating a mixture of methylal and acetone with gaseous hydrogen chloride, and then heating it with aniline and concentrated hydrochloric acid (Beyer, J. pr. Chem. 1886, [ii.] 33, 418; Meister, Lucius & Brüning, D. R.-P. 35133); also by distilling 2-hydroxylepidine with zinc dust (Knorr, Annalen, 1886, 235, 94); or by heating lepidine-2-carboxylic acid above its fusing-point (Koenigs and Mengel, Ber. 1904, 37, 1324).

Properties.—It is an oil, b.p. 265·5° under 746·7 mm., sp.gr. 1·0862 at 20° (Krakau, *cf.* Chem. Soc. Abstr. 1886, 50, 162), has the odour of quinoline, and is miscible in all proportions with alcohol, ether, benzene, or light petroleum. The *platinichloride* forms triclinic crystals, m.p. 226°–230° (Knorr, *l.c.*), the *picrate*, crystals, m.p. 212°–213° (Krakau, *l.c.*), the *methiodide*, prisms, m.p. 173°–174° (Hoogewerff and van Dorp, *l.c.*).

Reactions.—By chromic acid mixture it is oxidised to *cinchonic* (quinoline-4-carboxylic) *acid*, but with alkaline permanganate it gives *pyridine*-2 : 3 : 4-*tricarboxylic acid* (Hoogewerff and van Dorp, Ber. 1880, 13, 1640). Like quinaldine, it furnishes condensation products with aldehydes (Koenigs, Ber. 1898, 31, 2364; Loew, Ber. 1903, 36, 1166).

For *nitro-* and *amino-* derivatives, *sulphonic acids*, &c., *cf.* Koenigs, Ber. 1890, 23, 2669; Busch and Koenigs, *ibid.* 2679.

The 6-*methoxy-* derivative, m.p. 50°–52° (with 1 mol. H_2O), obtained when quinine is heated with caustic alkali, has been synthesised from *p*-anisidine, acetone and methylal (Pictet and Misner, Ber. 1912, 45, 1801). Like quinine, it gives a green coloration with chlorine water and ammonia (Koenigs, *l.c.*).

The toluquinolines, and many of their derivatives, have been obtained by Skraup's reaction (*cf.* Monatsh. 1885, 6, 761). The 5-, 7-, and 8-toluquinaldines, with hydrogen bromide and bromine, form compounds of the composition $B{\cdot}Br_2{\cdot}HBr$, which, when heated at 150°–200°, are converted into *ω-bromomethylquinolines* $C_{10}H_8N{\cdot}CH_2Br$. The 6- compound behaves differently (Claus, D. R.-P. 98272).

2 : 4-Dimethylquinoline, formed by the condensation of acetone and aniline in the presence of nitrobenzene and hydrogen chloride (Meister, Lucius & Brüning, D. R.-P. 32961; *cf.* Beyer, J. pr. Chem. 1886, [ii.] 33, 401), or of *o*-aminoacetophenone and acetone in caustic alkali solution (Fischer, Ber. 1886, 19, 1037), is an oil, b.p. 264°–265°, oxidised by chromic acid to 2-*methylquinoline*-4-*carboxylic acid* (Beyer, *l.c.*), but by permanganate to 2-*methylpyridine*-4 : 5 : 6-*tricarboxylic acid*.

Phenylquinolines.

Both in their mode of preparation and in many of their properties, the phenylquinolines show much resemblance to the alkylquinolines. Those containing the aryl group in the 2- or 3-position can be prepared by reactions similar to those employed by Doebner and Miller, or by Friedländer for alkylquinolines (*cf.* Doebner and Miller, Ber. 1883, 16, 1665; Friedländer and Göhring, *ibid.* 1835), and those containing it in the 6- or 8- position by Skraup's reaction (*cf.* La Coste and Sorger, Annalen, 1885, 230, 8). As radicles such as Cl, NO_2, NH_2, SO_3H, OH, and CO_2H may occur in the aryl group, in addition to substituents present in the quinoline complex, the number of phenylquinoline derivatives is large. Reference can be made here only to those which furnish dye-stuffs or are related to cinchona alkaloids.

2-Phenyl-4-methylquinoline (*flavoline*), obtained by heating flavenol with zinc dust (Fischer and Rudolph, Ber. 1882, 15, 1503), or *o*-aminoacetophenone with a solution of acetophenone in aqueous alcohol rendered alkaline with caustic soda (Fischer, Ber. 1886, 19, 1037), forms prisms, m.p. 64°–65°, b.p. 373°–375° (Bernthsen and Hess, Ber. 1885, 18, 34). On nitration with fuming nitric acid at 50°–60°, it gives the 4′-*nitro-* derivative, which has an odour of musk, and when reduced yields *flavaniline* (Besthorn and Fischer, Ber. 1883, 16, 68).

Flavaniline (2 : 4′-*aminophenyl*-4-*methylquinoline*) was first prepared by heating acetanilide with zinc chloride at 250°–270° (Fischer and Rudolph, Ber. 1882, 15, 1500; Meister, Lucius & Brüning, D. R.-P. 19766; Eng. P. 5427 of 1881), its constitution being ascertained partly from its conversion into flavenol by the diazo-reaction (Fischer and Rudolph, *l.c.*) and partly by its synthesis from a mixture of *o*-amino- and *p*-amino-acetophenone with zinc chloride at 100° (Fischer, Ber. 1886, 19, 1038).

It can also be obtained by heating aniline hydrochloride with acetic anhydride at 180°–200° (Baum, D. R.-P. 27948), or acetanilide hydrochloride at 280° (Noelting and Weingärtner, Ber. 1885, 18, 1341), or acetyl-*o*-aminobenzoic acid with dehydrating agents (Meister, Lucius & Brüning, D. R.-P. 21682; Eng. P. 1724 of 1882), or acetophenoneoxime with phosphoric oxide at 60° (Goldschmidt, Chem. Zeit. 1903, 27, 279).

Properties.—It crystallises in prisms, m.p. 97°, volatilises without decomposition, dissolves only very sparingly in water, and forms two series of salts, those with 1 mol. of a monobasic acid being yellowish-red, but those with 2 mols. colourless. The *hydrochloride* $C_{16}H_{14}N_2,HCl$ dyes silk and wool a bright yellow (Köchlin, Dingl. poly. J. 1884, 253, 86).

*iso*Flavaniline (2 : 2′-*aminophenyl*-4-*methylquinoline*), giving an intense yellow solution in

cold water or alcohol (Bischler and Burkart, Ber. 1893, 26, 1353), and 6-*amino*-4-*phenylquinoline* (Meister, Lucius & Brüning, D. R.-P. 79385) have been described.

Flavenol (2 : 4′-*hydroxyphenyl*-4-*methylquinoline*), obtained from flavaniline by the diazo-reaction, forms scales, m.p. 238°, dissolves only sparingly in alcohol, but readily in caustic soda solution, and is insoluble in ammonia. On distillation with zinc dust it yields *flavoline* (Fischer and Rudolph, *l.c.*).

1-Phenyl-4-hydroxy-2-quinolone (N-*phenyl*-4-*hydroxycarbostyril*), easily soluble in sodium carbonate solution, couples with diazotised bases (Meister, Lucius & Brüning, D. R.-P 287803). Of the three isomeric 4-phenolquinolines which have been synthesised, 4 : 2′-*hydroxyphenylquinoline* is a degradation product of *apo*cinchenine (Koenigs and Nef, Ber. 1887, 20, 622; Besthorn and Jaeglé, Ber. 1894, 27, 907; Meister, Lucius & Brüning, D. R.-P. 79173). Descriptions of the following aryl derivatives are also to be found in the Patent literature: 4 : 2′-, 4 : 3′- and 4 : 4′-*hydroxyphenylquinaldine* (Meister, Lucius & Brüning, D. R.-P. 80501); 6-*hydroxy*-4-*phenylquinaldine* (*ibid.* D. R.-P. 79871); 6-*methoxy*-4-*phenylquinaldine* (*ibid.* D. R.-P. 35133).

Quinolyl Alkyl Ketones.

For the preparation of quinoline compounds containing the radicle ·CH(OH)·CH·N: in the 4-position to which the specific effect of quinine in malaria has been attributed (*cf.* Kaufmann, Ber. 1913, 46, 58) 4-quinolyl alkyl ketones form a convenient source, inasmuch as from them by bromination, followed by interaction with an amine, β-aminoalkyl derivatives are obtained (Kaufmann, D. R.-P. 268931), from which by reduction with hydrogen and colloidal palladium the corresponding carbinols are formed (Kaufmann, D. R.-P. 283512). But of these products the nearest analogue described to quinine, *viz.* 6-*methoxy*-4-*quinolyl piperidinomethyl carbinol*, containing the group ·CH(OH)·CH_2·NC_5H_{10} in the 4-position, although an antipyretic, bitter to the taste and fluorescing blue in acid solution, is devoid of specific effect towards malaria (*cf.* Friedländer, Fortschritte Teerfarb. 11, 620).

2-**Quinolyl methyl ketone**, m.p. 52°, has the odour of orange blossoms, and the *ethyl* ketone, m.p. 58°–59°, that of jasmine (Givaudin and Kaufmann, D. R.-P. 280973; Kaufmann, D. R.-P. 282457). Both ketones are volatile with steam.

4-**Quinolyl methyl ketone**, prepared either by the interaction of 4-cyanoquinoline and magnesium methyl iodide, followed by decomposition with water (Kaufmann and Kunkler, Ber. 1912, 45, 3093; Kaufmann, D. R.-P. 276656; Eng. P. 9315 of 1913) or by saponifying ethyl quinolylacetate and eliminating the CO_2H group by distillation in a vacuum (Zimmer, D. R.-P. 268830), is a thick oil, m.p. below −20°, b.p. 138° under 2 mm., 99° under 0·08 mm., only slightly volatile with steam. The *acetate* forms needles, m.p. 70°, and the *picrate* yellow needles, decomp. 165°–170° (Kaufmann, *l.c.*); the *oximino*-derivative, needles, decomp. 237°–242°, yields the *amine* by reduction (Kaufmann, Kunkler and Peyer, Ber. 1913, 46, 63).

The 2-phenyl-4-quinolyl derivative forms yellow crystals, m.p. 75° (Chem. Ind. Basle, Brit. P. 185913). The 6-methoxy-4-quinolyl derivative, golden-yellow scales, m.p. 92°, gives solutions showing yellowish-green fluorescence (Kaufmann and Peyer, Ber. 1912, 45, 3098; Zimmer, D. R.-P. 268830); the *carbinol*, obtained from it by reduction, forms needles, m.p. 120°–121° (Zimmer, D. R.-P. 330813; *cf.* Chem. Soc. Abstr. 1921, i. 355), fluoresces blue in dilute sulphuric acid solution and develops an emerald-green coloration with chlorine water and ammonia (Kaufmann, Kunkler and Peyer, *l.c.*). From the *oxime*, m.p. 142°–150°, 6-*methoxy*-4-α-*aminoethylquinoline*, b.p. 169°–171° under 2 mm., is obtained by reduction with hydrogen and palladium black (Zimmer, D. R.-P. 285637).

4-**Quinolyl ethyl ketone**, an oil, b.p. 163°–166° under 8–9 mm., 170°–174° under 12 mm., gives an *acetate*, m.p. 87° (Rabe and Pasternack, Ber. 1913, 46, 1031; Zimmer, D. R.-P. 280970).

Cyanoquinolines.

2-**Cyanoquinoline** has m.p. 94°, b.p. 150°–160° under 23 mm. (Givaudin and Kaufmann, D. R.-P. 280973).

4-**Cyanoquinoline**, formed when cinchonamide is dehydrated by thionyl chloride or phosphoric oxide (Meyer, Monatsh. 1902, 23, 904) or when 4-cyanoquinoline methiodide, obtained from quinoline methiodide, is heated at 210°–220° in a current of carbon dioxide (Kaufmann and Widmer, Ber. 1911, 44, 2062), sublimes in long needles, m.p. 95°. Reduced in hydrochloric acid solution by hydrogen and colloidal palladium, it yields 4-ω-*aminomethylquinoline*, b.p. 172° under 8 mm. (Zimmer, D. R.-P. 279193).

The 2-phenyl- derivative, obtained by heating 2-phenylcinchonamide at 365° until elimination of water ceases, forms needles, m.p. 140° (Bayer, D. R.-P. 288243).

Quinolinecarboxylic Acids.

Quinolinemonocarboxylic acids, of which all the seven isomerides are known, can be prepared by the following general methods:—

(*a*) For those containing the CO_2H group in the 'pyridine' ring: either by oxidation of the corresponding methylquinoline, or by synthetical methods;

(*b*) For those containing it in the 'benzene' ring: either by Skraup's method, or by hydrolysis of the nitrile obtainable from the corresponding amino- derivative by Sandmeyer's method or from the sulphonic acid by distillation with potassium cyanide.

Oxidation of the alkylquinolines is usually effected by means of chromic acid in dilute sulphuric acid, as the action, although slow, is limited to the alkyl groups. With permanganate the 'benzene' ring is ruptured, leading to the production of pyridinecarboxylic acids, except in the case of 2-alkylquinolines, when acyl derivatives of anthranilic acid are obtained.

The quinolinecarboxylic acids are crystalline, readily lose carbon dioxide when heated with lime, and form stable salts both with bases and acids. In many cases they form quaternary

ammonium compounds with alkyl iodides, from which betaïnes and not hydroxides result by interaction with silver oxide and water. The only acids which call for detailed mention here are the 2- and the 4- derivatives.

Quinoline-2-carboxylic acid (*quinaldic acid*) is obtained by oxidation either of quinaldine with chromic acid in dilute sulphuric acid (Doebner and Miller, Ber. 1883, 16, 2472), or of 2-quinolylethanol (formed by the condensation of quinaldine and formaldehyde) with nitric acid of sp.gr. 1·4 (Besthorn and Ibele, Ber. 1906, 39, 2329). The *acid*, $HA+2H_2O$, forms needles, m.p. (anhydrous) 156°; the *chloride*, needles, m.p. 97°–98° (*cf. inter alia*, Besthorn and Ibele, Ber. 1905, 38, 2127; 1906, 39, 2329; Besthorn, Ber. 1909, 42, 2697; Meyer and Turnau, *ibid.* 1166). When the acid is heated at 130°–135° with acetic anhydride, or the chloride interacts with quinoline in the cold, a red dye $C_{19}H_{12}ON_2$, m.p. 230°–240°, is obtained (Besthorn and Ibele, Ber. 1904, 37, 1236; 1905, 38, 2127; Besthorn, Ber. 1908, 41, 2001; D. R.-P. 168948).

Quinoline-4-carboxylic acid (*cinchonic acid*) is the chief product (50 p.c.) obtained by oxidising cinchonine with chromic acid (Koenigs, Ber. 1879, 12, 97; 1894, 27, 1501); and is formed similarly from cinchonidine, cinchotenine, cinchotenidine (Skraup, Ber. 1879, 12, 230; Annalen, 1880, 201, 303) or lepidine, (Hoogewerff and van Dorp, Rec. trav. chim. 1883, 2, 10). For a synthesis from 4-cyanoquinoline methiodide, *cf.* Kaufmann, Ber. 1918, 51, 119. The *acid*, $HA+H_2O$, forms needles, or $HA+2H_2O$, monoclinic or triclinic prisms, m.p. (anhydrous) 253°–254°; and the *chloride*, needles, m.p. 170° (Meyer, Monatsh. 1901, 22, 109). On nitration it yields 5-*nitrocinchonic acid*, from which by reduction the *peri*- anhydride of 5-aminocinchonic acid, m.p. 254°–255°, is obtained (Koenigs and Lossow, Ber. 1899, 32, 717).

Quinic acid (6-*methoxycinchonic acid*), obtained when quinine is oxidised with chromic acid (Skraup, Ber. 1879, 12, 230, 1104), has been synthesised from *p*-anisidine, methylal, and ethyl pyruvate (Pictet and Misner, Ber. 1912, 45, 1801). It forms prisms, m.p. 280°, and in alcoholic, but not in aqueous solution, shows blue fluorescence.

Arylcinchonic Acids.

Whereas cinchonic acid is without influence on the elimination of uric acid from the system, its 2-phenyl derivative (*atophan*) exhibits this property in a marked degree (Ciusa and Luzzatto, Chem. Soc. Abstr. 1913, i. 682, 1418; Folin and Lyman, *ibid.* 1914, i. 115), but has a persistent bitter taste and gives rise to certain undesirable after-effects when administered. These disadvantages are less prominent or non-existent in derivatives of 2-phenylquinoline-4-carboxylic acid, but their suppression is associated with the diminution or loss of the specific effect on the excretion of uric acid.[1] For example, as illustrating the influence of substituents in the quinoline complex on uric acid elimination,[1] methyl in the 6-position (*paratophan* and its ethyl ester, *novatophan*) and methoxyl in the 8-position (*isatophan*) diminish it, but methoxyl or the amino-group in the 6-position inhibit it (Ciusa and Luzzatto, *l.c.*), while substitution of groups other than methyl in the phenyl radicle [2] also impairs the activity of atophan in this direction (Impens, Chem. Soc. Abstr. 1914, i. 459).

2-**Phenylquinoline-4-carboxylic acid**, obtained by heating an alcoholic solution of aniline, pyruvic acid and benzaldehyde in mol. prop. on a water bath for 3 hours (Doebner and Gieseke, Annalen, 1887, 242, 291) or of benzylideneaniline and pyruvic acid in mol. prop. (Garzarolli-Thurnlackh, Ber. 1899, 32, 2276; *cf.* Schering, Eng. P. 15684 of 1912; 11836 of 1914), is formed in almost quantitative yield when a mixture of isatin (5 pts.), acetophenone (4 pts.), and 33 p.c. caustic potash solution (20 pts.) is stirred during 8 hours on a water bath (Kalle, D. R.-P. 287304; Eng. P. 17725 of 1914; *cf.* Pfitzinger, J. pr. Chem. 1897, [ii.] 56, 292; Bayer, Eng. P. 19844 of 1912), or when 20 p.c. ammonia is used as the alkali, the mixture heated at 130° and the resulting amide hydrolysed by concentrated sulphuric acid at this temperature (Bayer, D. R.-P. 290703).

It crystallises in needles, m.p. 208°–209° (Pfitzinger, *l.c.*), 212°–213° (Boehm and Bournot, Ber. 1915, 48, 1570), giving 2-phenylquinoline at higher temperatures, is almost insoluble in water or 15 p.c. caustic soda solution, but dissolves in 20 pts. of ethyl and 25 pts. of methyl alcohol, 35 pts. of acetone and 250 pts. of benzene, each at the boiling-point (Boehm and Bournot, *l.c.*). From a cold solution of its sodium salt carbon dioxide separates a yellow crystalline compound $(C_{16}H_{10}O_2N)_2NaH+H_2CO_3$ (Schering, D. R.-P. 285499). The *methyl* ester, prisms, m.p. 61° (Claus and Brandt, Annalen, 1894, 282, 106; Schering, D. R.-P. 275963) and *ethyl* ester (*acitrin*), prisms, m.p. 61°–62°, are bitter to the taste; the iso*amyl* ester, oil, b.p. 235°–240° under 2 mm. (Schering, D. R.-P. 287959); *allyl* ester, m.p. 30°, b.p. 260° under 15 mm. (Chem. Ind. Basle, Brit. P. 150401; Rosenmund, Ber. 1921, 54, [*B*] 2894); *phenyl* and *β-naphthyl* esters (Schering, D. R.-P. 244788) and *salicyl* ester, scales, m.p. 188° (Bayer, D. R.-P. 261028), are tasteless. For other tasteless esters, *cf.* Schering, D. R.-P. 249766; 267208; Eng. P. 16483 of 1913; Bayer, D. R.-P. 267209. The *amide*, needles, m.p. 199°, is destitute of taste (Schering, D. R.-P. 252643; Bayer, D. R.-P. 290703). The *sulphonic acid* is crystalline (Schering, D. R.-P. 270994; Eng. P. 16482 of 1913).

2-α-Naphthylquinoline-4-carboxylic acid, needles, m.p. 198°, and the β-compound, m.p. 234°, share the properties of the 2-phenyl-derivative (Schering, D. R.-P. 284232).

[1] 2-*Phenyl*-β-*naphthaquinoline*-4-*carboxylic acid* (diapurin) and 2 : 4′-*hydroxy*-3′-*carboxyphenylquinoline*-4-*carboxylic acid* (hexophan), both resemble atophan in its specific effect, the former being the more easily tolerated (Doebner and Kuntze, Annalen, 1888, 249, 129; Ciusa and Luzzatto, *l.c.*), and the latter having a sweet taste (Meister, Lucius & Brüning, D. R.-P. 293467; Eng. P. 22828 of 1914).

[1] Among substituents in the quinoline complex examined in this connexion are 3-*phenyl* (Bayer, D. R.-P. 249765), 6-*methyl* (Doebner and Gieseke, Annalen, 1887, 242, 296), 6-*iodo* (Schering, D. R.-P. 288303), 6-*amino* (Meister, Lucius & Brüning, D. R.-P. 287804, 288865), 6-*methoxy* and 8-*methoxy* (Doebner, Annalen, 1888, 249, 105).

[2] Among substituents in the phenyl group examined in this connexion are 2′-, 3′- and 4′-*amino* (Schering, D. R.-P. 279195; 287216) and 2′-, 3′- and 4′-*hydroxy* (Kalle, D. R.-P. 284233).

2-Piperonylquinoline-4-carboxylic acid, m.p. 215°, its esters, amide and arylamides do not promote the elimination of uric acid (Schering, D. R.-P. 244497; 277438; 281097; 281136; 281603; Eng. P. 14128 of 1913). 2-Antipyrylquinoline-4-carboxylic acid, m.p. 266°–268°, has been described (Meister, Lucius & Brüning, D. R.-P. 270487).

Tetrahydro- Derivatives.

(i.) **Tetrahydroquinoline** is obtained from quinoline by reduction with zinc and hydrochloric acid (Wyschnegradsky, Ber. 1879, 12, 1481), tin and hydrochloric acid (Wagner, Ber. 1880, 13, 2400; Hoffmann and Koenigs, Ber. 1883, 16, 728), sodium amalgam (Koenigs, Ber. 1881, 14, 100), sodium and alcohol (Weidel and Gläser, Monatsh. 1886, 7, 328), or electrolytically in dilute sulphuric acid solution (Ahrens, *cf.* Chem. Soc. Abstr. 1897, 72, i. 369; Merck, D. R.-P. 90308; 104664; Eng. P. 21471 of 1898). It is also formed from 2-hydroxyquinoline by reduction with sodium and alcohol (Knorr and Klotz, Ber. 1886, 19, 3302). To isolate the base, the reduction product, if acid, is made alkaline and distilled with steam; tetrahydroquinoline and unchanged quinoline pass over, and the former is precipitated as hydrochloride by passing hydrogen chloride into a dry ethereal extract of the distillate (Hoffmann and Koenigs, *l.c.*).

Properties.—It is an oil, which solidifies in a freezing mixture, b.p. 251° (corr.), sp.gr. 1·0627 at 15°/15° (Perkin, Chem. Soc. Trans. 1896, 69, 1214), and has the properties of a secondary alkylated aniline (*cf.* Bamberger and Wulz, Ber. 1891, 24, 2055). It is oxidised to quinoline by nitrobenzene (Lellmann and Reusch, Ber. 1889, 22, 2390), mercuric oxide (Tafel, Ber. 1892, 25, 1622), silver nitrate (Ber. 1894, 27, 824), or iodine (Schmidt, Arch. Pharm. 1899, 237, 561). The 'piperidine' ring of its quaternary ammonium derivatives is not ruptured by the Hofmann method, but by reduction with sodium amalgam and water (Emde, Annalen, 1912, 391, 90). Its *benzoyl* derivative, m.p. 75°, on oxidation by permanganate yields *benzoylisatic acid* (Hoffmann and Koenigs, *l.c.*). The *hydrochloride* forms needles, m.p. 180° (Friedländer and Ostermaier, Ber. 1882, 15, 335).

1-Methyltetrahydroquinoline, obtained either by methylation of tetrahydroquinoline (Hoffmann and Koenigs, Ber. 1883, 16, 732), or by reduction of tetrahydroquinoline methiodide with tin and hydrochloric acid (Feer and Koenigs, Ber. 1885, 18, 2388), or, mixed with 2-methylquinoline, by the action of caustic alkali solution on quinoline methiodide (Decker, Ber. 1903, 36, 2568), is an oil, b.p. 242°–244° under 720 mm., sp.gr. 1·022 at 20/°4°, which resembles dimethylaniline in many of its properties. The *sulphate*, **Kairoline,** was at one time used as an antipyretic; the *picrate* forms yellow needles, m.p. 144·5° (Decker, *l.c.*).

2-Methyltetrahydroquinoline (*tetrahydroquinaldine*), obtained by reducing quinaldine by tin and hydrochloric acid (Doebner and Miller, Ber. 1883, 16, 2467), is an oil, b.p. 250° corr., sp.gr. 1·042 at 16°/4° (Ladenburg, Ber. 1894, 27, 77). The base has been resolved into its optical antipodes (Pope and Peachey, Chem. Soc. Trans. 1899, 75, 1066; Pope and Read, *ibid.* 1910, 97, 2199).

(ii.) 6-**Hydroxytetrahydroquinoline,** formed by reducing 6-hydroxyquinoline with tin and hydrochloric acid, is crystalline, m.p. 148°; its *acetyl* derivative crystallises in needles, m.p. 82° (Badische, D. R.-P. 42871).

Its methyl ether, **thalline,** $C_9H_{10}N{\cdot}OCH_3$, formed when 6-methoxyquinoline is reduced by tin and hydrochloric acid (Badische, D. R.-P. 30426; Skraup, Monatsh. 1885, 6, 767), or 6-hydroxytetrahydroquinoline is methylated by any of the ordinary processes (Badische, D. R.-P. 42871), forms rhombic prisms, m.p. 42°–43°, b.p. 283° under 735 mm., and dissolves only very sparingly in cold water, but readily in alcohol. The aqueous solutions of its salts are coloured an intense green by ferric chloride, chlorine water, or other oxidising agents. Of these salts, the *sulphate*, $B_2{\cdot}H_2SO_4+2H_2O$, needles, soluble in 5 pts. of water at the ordinary temperature; and the *tartrate*, $B{\cdot}C_4H_6O_6$, prisms, soluble in 10 pts. of water at 15°, were at one time employed as antipyretics.

(iii.) 8-**Hydroxytetrahydroquinoline,** obtained by reduction of 8-hydroxyquinoline with tin and hydrochloric acid, crystallises in needles, m.p. 121°–122°, is not volatile with steam, and dissolves fairly readily in hot water (Bedall and Fischer, Ber. 1881, 14, 1368). Both this base and its 1-alkyl derivatives can be used as photographic developers (Lembach and Schleicher, D. R.-P. 86978, 89181).

The 1-methyl derivative, $OH{\cdot}C_9H_9N{\cdot}CH_3$, **Kairine,** prepared by mixing carefully the tetrahydro- base with methyl iodide, and completing the reaction in a reflux apparatus (Fischer, Ber. 1883, 16, 714; D. R.-P. 21150; Eng. P. 3044 of 1882), crystallises from alcohol in prisms, m.p. 114°, dissolves only sparingly in water, but readily in warm alcohol, and in alcoholic solution gives with ferric chloride a deep brown coloration. The readily soluble *hydrochloride*. $B{\cdot}HCl+H_2O$, was at one time employed as a febrifuge.

The 1-ethyl derivative, which closely resembles the 1-methyl compound, forms monoclinic prisms, m.p. 76° (Fischer, Ber. 1883, 16, 717; Fischer and Renouf, Ber. 1884, 17, 756). Similarly, its *hydrochloride*, B·HCl (Kairine A), has antipyretic properties.

Quaternary Ammonium Compounds.

Quaternary ammonium (quinolinium) compounds are obtained by the combination of quinoline, its homologues, and the greater number of its derivatives, with alkyl iodides.

Quinoline methiodide (*methylquinolinium iodide*), obtained from a solution of dry quinoline and methyl iodide in benzene either kept in the cold (Kaufmann and Albertini, Ber. 1909, 42, 3779), or heated in an efficient reflux apparatus (Marckwald and Meyer, Ber. 1900, 33, 1884; Decker, *ibid.* 2276), forms yellow crystals, m.p. 133°, which separate from dilute alcohol as the hydrate $C_{10}H_{10}NI+H_2O$, m.p. 72° (Decker, Ber. 1903, 36, 1205, 2568). The ethiodide forms yellow needles, m.p. 158°–160° (Hoogewerff and van Dorp. Rec. trav. chim. 1883, 2, 321), and when heated at 280°–290° is converted into a mixture of 2- and 4-*ethylquinoline* with diethylquinoline (Reher, Ber. 1886, 19, 2996).

Quinaldine methiodide (*methylquinaldinium*

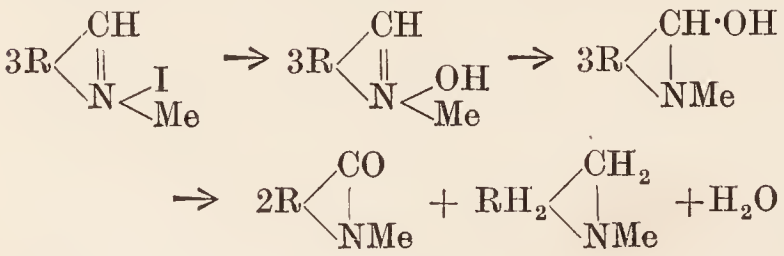
iodide) crystallises from alcohol in long, citron-yellow needles, m.p. 195°, and dissolves easily in cold water but is insoluble in ether (Doebner and Miller, Ber. 1883, 16, 2468). The ethiodide forms straw-coloured needles, sparingly soluble in water, decomp. at 226° (Spalteholz, Ber. 1883, 16, 1851), m.p. 234° with decomp. (Pictet and Bunzl, Ber. 1889, 22, 1848).

Lepidine methiodide (*methyllepidinium iodide*) crystallises from alcohol in yellow prisms, m.p. 173°–174° (Hoogewerff and van Dorp, Rec. trav. chim. 1883, 2, 318). The ethiodide forms prisms, m.p. 141°–143° (*ibid.* 321).

Cyanine Dyes.

From the alkylquinolinium iodides two types of compound can be obtained by interaction with caustic alkali. These are the quinolones and the quinocyanines, the last-named being dye-stuffs which—although too fugitive for ordinary dyeing purposes—are valuable as sensitisers in photographic work. The conditions under which they are formed are given in the following sections: I (quinolones), II (quinocyanines).

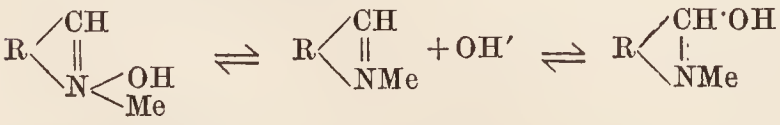
I. When alkylquinolinium iodides and their substitution derivatives interact with aqueous caustic soda to which ferricyanide has been added, *alkylquinolones*, volatile with steam, insoluble in water but soluble in alcohol or ether, are produced (Decker, J. pr. Chem. 1892, [ii.] 45, 161; Ber. 1892, 25, 443). Bases insoluble in water are also obtained as a rule [1] when interaction takes place between these iodides and the alkali [2] without the addition of ferricyanide (La Coste, Ber. 1882, 15, 194; Decker, Ber. 1891, 24, 691; J. pr. Chem. *l.c.*), but the products are mixtures of alkylquinolone with alkyltetrahydroquinoline,[3] the course of the reaction in the absence of the oxidising agent being probably as follows (R=C_8H_6)



(Decker, Ber. 1892, 25, 3326; 1903, 36, 1212, 2568).

[1] The degree of readiness with which this reaction takes place is greatly influenced by substituents, such as NO_2, NH_2, etc., present in the molecule (*cf.* Decker and Kaufmann, J. pr. Chem. 1911, [ii.] 84, 441).

[2] With a suspension of silver oxide in water in the place of aqueous caustic soda, a strongly alkaline solution is obtained from which the iodide may be regenerated, but on exposure to the air decomposes with the separation of a similar precipitate simultaneously with enfeeblement of the basicity (La Coste, *l.c.* 191; *cf.* Hantzsch and Kalb, Ber. 1899, 32, 3119; Decker, Ber. 1902, 35, 2592). The change of quinolinium hydroxide into carbinol base (*pseudo*ammonium base) may be represented thus:



cf. also, Decker, Ber. 1892, 25, 3326).

[3] The view advocated by Kaufmann that the final products are aminoaldehydes (*cf.* Kaufmann and Strübin, Ber. 1911, 44, 682; Kaufmann and Plá y Janini, *ibid.* 2670) has been abandoned in favour of Decker's interpretation of the reaction (Decker and Kaufmann, J. pr. Chem. 1911, [ii.] 84, 228, 231).

II. By the substitution of methyl alcohol as solvent for the alkali in place of water, the end product of the reaction is a quinocyanine, the nature of which depends on the bases used in its production—whether quinoline, quinaldine, lepidine or mixtures of any two of these—and on the conditions employed.

Under the general heading quinocyanines, the term adopted by König for purposes of classification (Ber. 1922, 55, [*B*] 3306), are included the *apo*cyanines (the yellow xantho- and red erythro-cyanines), cyanines, *iso*cyanines, carbocyanines, dicyanines and cryptocyanines. In addition, there are benzothiazole dyes—the thiocyanines and carbothiocyanines—and the thio*iso*cyanines of mixed type containing both a benzothiazole and a quinoline complex.

History.—The first cyanine or quinoline-blue was prepared by Greville Williams, who obtained it by the action of caustic alkali on the product formed by heating quinoline (from cinchonine, but not from coal-tar) with amyl iodide (Trans. R. S. Edin. 1856, 21, 377; Chem. News, 1863, 2, 219). Hofmann showed it to be a derivative of quinoline and lepidine (Roy. Soc. Proc. 1863, 12, 410), and Hoogewerff and van Dorp, who showed the reaction to be one of condensation between an alkylquinolinium iodide and an alkyllepidinium iodide in molecular proportion, gave to dyes of this class the formula $C_{19}H_{13}N_2XYI$ (in which X and Y are alkyl groups), representing the cyanine reaction thus:

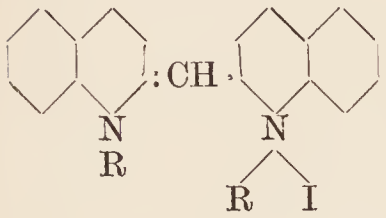
$$C_9H_7NXI+C_{10}H_9NYI+KOH = C_{19}H_{13}N_2XYI+KI+H_2O+H_2$$

They also found that while cyanines which are blue dyes result from the condensation of quinoline with lepidine, reddish-violet *iso*cyanines are formed from that with quinaldine (Rec. trav. chim. 1883, 2, 28; 1884, 3, 317; *cf.* Spalteholz, Ber. 1883, 16, 1847).

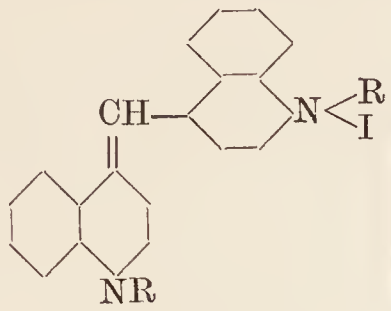
The discovery that ethyl red, the *iso*cyanine produced by condensing ethylquinolinium iodide with ethylquinaldinium iodide, sensitises dry photographic plates fairly evenly from the ultra-violet to the orange when stained with it (Miethe, Chem. Ind. 1903, 26 [3] 54), brought about the introduction of still more efficient sensitisers, *e.g.* pinaverdol, belonging to this group, by the use of which sensitiveness could be extended into the red (*cf.* Meister, Lucius & Brüning, D. R.-P. 167159, 167770; Eng. P. 9598 of 1903; Bayer, D. R.-P. 158078, 170048, 170049; Eng. P. 25144 of 1903). Two years later, dyes of the type to which pinacyanol belongs—obtained by condensing quinolinium with quinaldinium salts in the presence of formaldehyde—were found to be more effective than the *iso*cyanines, sensitising much further into the red (*cf.* Meister, Lucius & Brüning, D. R.-P. 172118, 175034, 178688, 189942, 200207; Eng. P. 16227 of 1905): these were classified later as carbocyanines by Mills and Pope (Phot. J. 1920, 60, 184). At the outbreak of the War the production of these sensitisers was wholly in German hands, but intensive methods, devised for their preparation and improvement in the chemical laboratories of Cambridge University, and later in America, overcame the shortage and incidentally led to a comprehensive survey of this group of dyes.

Constitution.—Decker's investigation of the

reactions leading up to the formation of alkylquinolones from alkylquinolinium iodides (*supra*) led him to regard the carbinol bases as intermediate compounds in the production of cyanines and to assign to these dyes formulæ of the type I (Ber. 1891, 24, 692 ; J. pr. Chem. 1911, [ii.] 84, 235).

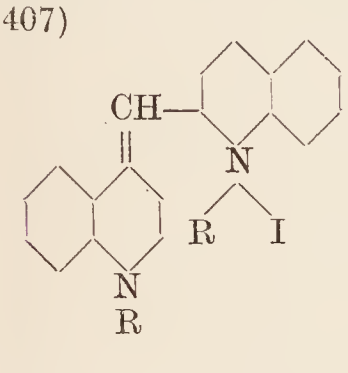


I. Cyanine (Decker) ; *Pseudoisocyanine* (Fischer and Scheibe).[1]

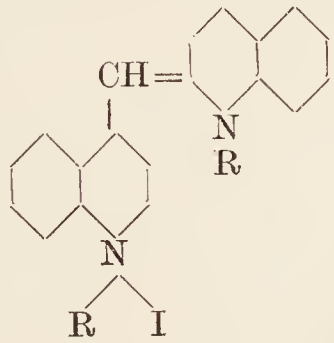


II. Cyanine (König).

The fact that lepidine is used in the production of cyanines and quinaldine in that of *iso*cyanines finds expression in the formulæ II and III adopted respectively for these substances—formulæ accepted a few years later by Kaufmann and Vonderwahl as the best representation of their own and of earlier work (Ber. 1912, 45, 1407)



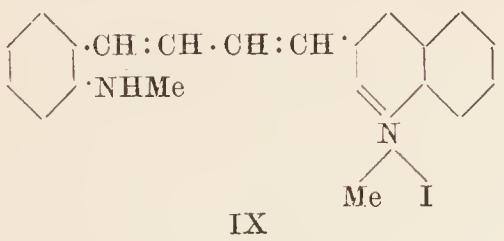
III. *Isocyanine* (König).[2]



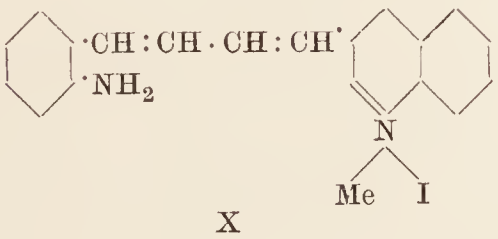
IV. *Isocyanine* (Mills and Wishart).

[1] Synthesised from 2-iodoquinoline methiodide and quinaldine methiodide (J. pr. Chem. 1920, [ii.] 100, 89).

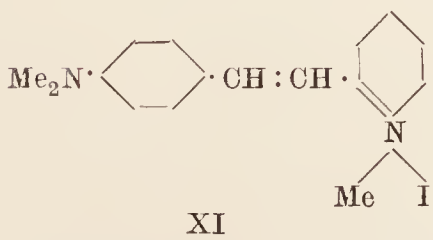
[2] In order to test the validity of the open chain formula IX suggested in 1912 by König for *iso*cyanine, Mills and Evans synthesised *o*-aminocinnamylidenequinaldine methiodide (X) and found it to be a reddish-brown dye for silk, but devoid of sensitising action on a gelatino-bromide plate (Chem. Soc. Trans. 1920, 117, 1136)



IX



X

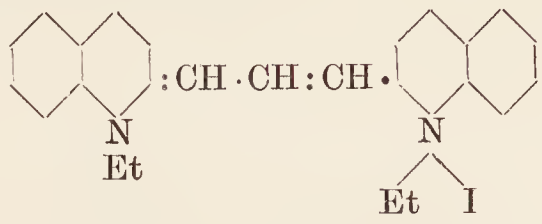


XI

This fact is remarkable in view of the synthesis of 2-*p*-dimethylaminostyrylpyridine methiodide (XI), an orange-yellow dye for silk which proves to be the most powerful sensitiser of gelatino-bromide plates yet known for green light (Mills and Pope, Chem. Soc. Trans. 1922, 121 946).

As the result of a study of the oxidation products of dimethyl*iso*cyanine, Mills and Wishart have shown that König's formula III for the *iso*cyanines must be replaced by IV : the two are obviously closely related, and there is reason to suppose that they represent virtually tautomeric substances (Chem. Soc. Trans. 1920, 117, 582).

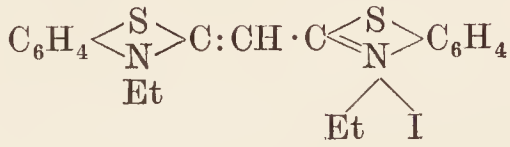
For the carbocyanines, formulæ have been proposed by Fischer (J. pr. Chem. 1918, [ii.] 98, 204) and by Wise, Adam, Stewart and Lund (J. Ind. Eng. Chem. 1919, 11, 460), but these are shown to be inadequate by Mills and Hamer (Chem. Soc. Trans. 1920, 117, 1551), who, from consideration of the products formed by oxidising pinacyanol, draw the conclusion that this dye is the *streptovinyl* derivative V of the cyanine I formulated by Decker.



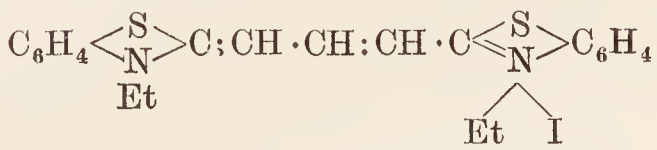
V. Pinacyanol (Mills and Hamer).

Confirmation of this view is afforded by König's synthesis of pinacyanol by the condensation of ethylquinaldinium iodide with ethyl orthoformate in the presence of acetic anhydride (Ber. 1922, 55, [*B*] 3303).

The marked resemblance shown by bases of the benzothiazole series with quinoline and quinaldine induced Hofmann to attempt the condensation of benzothiazole with methylbenzothiazole (Ber. 1887, 20, 2262). The product thus obtained, on re-examination by Mills, who condensed the ethiodides in pyridine solution, proved to be a mixture of a bright yellow and a purple dye belonging respectively to the *iso*cyanine, VI, and carbocyanine, VII, types, of which the former is the benzothiazole analogue of the quinoline derivative I (Chem. Soc. Trans. 1922, 121, 455).

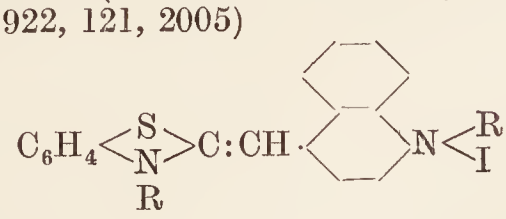


VI. Bright yellow dye. Thiocyanine.



VII. Purple dye. Carbothiocyanine.

These thio-compounds, together with the thio*iso*cyanines VIII (Braunholtz and Mills, Chem. Soc. Trans. 1922, 121, 2005)

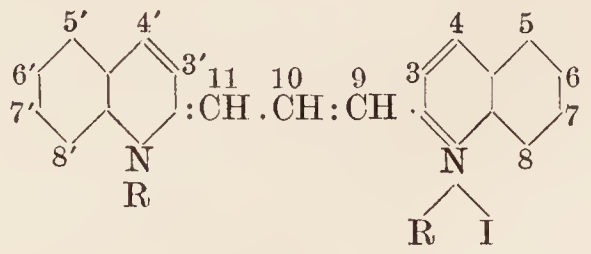


VIII.

obtained from a mixture of methylbenzothiazole and alkylquinolinium iodides are powerful photographic sensitisers.

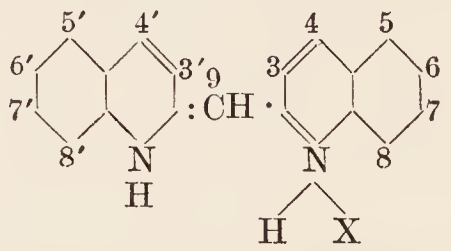
Nomenclature.—The position of substituents in the formulæ of the various types of cyanine dyes is indicated by a system of numbering

which begins with the quinquevalent nitrogen atom, the positions in a carbocyanine for example being numbered thus:



XII.

To avoid the use of prefixes such as *iso-*, carbo-, *pseudo-*, crypto- for distinguishing the different types, König suggests that as the constitution of this series of compounds has been largely elucidated, Fischer's term *quinocyanine* should be adopted for the parent substance, a non-methylated salt of Scheibe's quinolyldihydroquinolylmethane (Ber. 1922, 55 [*B*], 3307).



The three types, 2 : 2′-, 2 : 4′- and 4 : 4′ quinocyanines, include all the dyes of the group, except the *apo*cyanines which are 2 : 3′- derivatives, further types being provided by the introduction of vinylene groups between the quinoline residues, as indicated in the name 1 : 1′-dialkyl-*strepto*vinylene-2 : 2′-quinocyanine iodide for the carbocyanine XII. formulated above.

Apo*cyanines.*

*Apo*cyanines [1] are formed when an alkylquinolinium iodide (1 mol.) is heated with caustic alkali ($\frac{1}{2}$–$\frac{2}{3}$ mol.) in alcoholic solution, the *xantho*apo*cyanine* (which is the minor product) separating in yellow crystals as the solution cools, and later the *erythro*apo*cyanine* in red needles of coppery lustre. These dyes are distinguished from the cyanines by the slowness with which their aqueous solutions are decolorised by acids. The xantho*apo*cyanines in alcoholic solution show yellowish-green fluorescence and with alkalis give precipitates characterised by blue fluorescence when dissolved in alcohol or concentrated sulphuric acid (Kaufmann and Strübin, Ber. 1911, 44, 494; *cf.* Decker and Kaufmann, J. pr. Chem. 1911, [ii.] 84, 239; Meister, Lucius & Brüning, D. R.-P. 154448).

Cyanines.

Cyanines (4 : 4′-quinocyanines) are obtained by condensing an alkylquinolinium iodide with an alkyllepidinium iodide by the aid of caustic alkali in alcoholic solution. They form almost opaque greenish crystals, give solutions in alcohol which are blue by reflected and violet by transmitted light, but become colourless on acidification, and are the monacid salts of diacid bases, B·HX, the normal salts B·2HX being colourless. On silk they give very beautiful blue shades, but being fast neither to light nor acids are valueless as dyes. To Vogel is due the observation that cyanines act as sensitisers for the photographic plate (Ber. 1875, 8, 1635), but their disuse followed the discovery that unlike them *iso*cyanines do not cause fogging and give a continuous sensitising band unbroken in the green.

Iso*cyanines.*

*Iso*cyanines (2 : 4′-quinocyanines) are produced by the interaction of an alkylquinolinium iodide with an alkylquinaldinium iodide in alcoholic solution in the presence of caustic alkali.[1] Included in this group are the photographic sensitisers known under trade names as *ethyl red*, *pinachrome*, and *pinaverdol* or *sensitol green*. For details of preparation, properties and sensitising action reference must be made to original sources (*cf.* Wise, Adams, Stewart and Lund, J. Ind. Eng. Chem. 1919, 11, 460; Mills and Pope, Phot. J. 1920, 60, 186; Hamer, Chem. Soc. Trans. 1921, 119, 1432). The crystals are often striated, show a green metallic reflex, and exhibit marked pleochroism. In solution they give redder shades than the cyanines, and as dyes on silk are equally fugitive. As summarised by Mills and Pope from the results of an investigation of 20 *iso*cyanine dyes (*l.c.*), the sensitising effect conferred by methyl or ethyl groups in the 1 : 1′-compounds is enhanced when a third methyl or ethyl group respectively is introduced in the 6- position, but depressed in the 2-position. Entry of the amino- group into the 5-, 6- or 6′- position in 1 : 1′-dimethyl*iso*cyanine iodide markedly augments the sensitising power, but if acetylated an opposite effect is observed, the depression being most marked for the 5-position, less so for the 6-position, and comparatively slight for the 6′-position. If cyanogen or phenyl be present in the 2′-position, the depression in sensitising power associated with the methyl group (*supra*) becomes so pronounced as practically to annul the strong sensitising action of the parent substance. Among the 20 *iso*cyanines examined by Mills and Pope, the extreme of sensitisation extended to about λ6600.

Carbocyanines.

The carbocyanines (*strepto*vinylene-2 : 2′-quinocyanines) are formed by the condensation of an alkylquinaldinium iodide (2 mols.) and formaldehyde (1 mol.) in the presence of alcoholic caustic alkali solution; nevertheless, in some cases—particularly in that of ethylquinaldinium iodide used in the production of pinacyanol—a better yield is obtained when ethylquinolinium iodide, which takes no obvious part in the reaction, is also present. Included in the group is the valuable sensitiser known by its trade name of *pinacyanol* or *sensitol-red*. For details of preparation, properties, and sensitising power of members of the group,[2] papers published

[1] According to König, the xantho- and erythro-*apo*cyanines are respectively 3 : 2′- and 3 : 4′-*apo*-quinocyanines (Ber. 1922, 55 [*B*], 3307).

[1] Adams and Heller state that an *iso*cyanine (4 : 2′-quinocyanine) isomeric with that from quinaldinium ethiodide is obtained when lepidinium ethiodide, free from quinoline and quinaldine, is boiled with a solution of caustic soda in methyl alcohol (J. Amer. Chem. Soc. 1920, 42, 2390).

[2] Homologues obtained from arylated derivatives of quinaldine are termed by Fischer pseudo*dicyanines* (J. pr. Chem. 1918, [ii.] 98, 223). With alkylated quinaldines containing methyl in the 4- position mixtures of these dyes with *dicyanines* may be obtained,

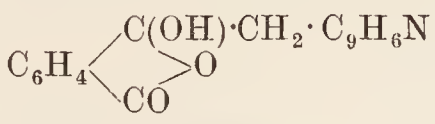
by Wise, Adam, Stewart and Lund (*l.c.*), Mills and Pope (Phot. J. 1920, 60, 256), and Braunholtz (Chem. Soc. Trans. 1922, 121, 170) should be consulted. Reviewing the results of an investigation of seventeen carbocyanines, Mills and Pope describe the iodides as sparingly soluble compounds, which are best crystallised from methyl alcohol: the crystals in bulk exhibit various shades of bluish-green and are usually associated with alcohol of crystallisation often obstinately retained. The solutions in methyl alcohol are deep blue in colour and show characteristic absorption spectra which correspond roughly with the two maxima of sensitisation conferred by the dyes. Introduction of the vinylene group, involving replacement of the :CH· coupling of the *iso*cyanines by the conjugated group: CH·CH:CH· of the carbocyanines leads to an extension of the sensitising effect far into the red region of the spectrum, the extreme limit of sensitisation observed reaching to about λ7000. The presence of substituents in the 5- and 5′-positions exercises a marked depressing effect on sensitising power, as does also the acetyl group on that conferred by amino-compounds.

Cryptocyanines.

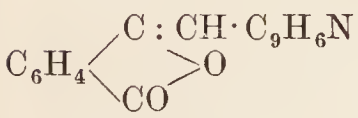
Cryptocyanines (probably *strepto*vinylene-4:4′-quinocyanines) are produced by substitution of lepidinium for quinaldinium compounds in the carbocyanine condensation with formaldehyde (Adams and Haller, J. Amer. Chem. Soc. 1920, 42, 2662). The dye, KIII, formed from lepidinium ethiodide is a purplish-black or bronze powder, and is a better sensitiser than the dicyanines as far as λ8500 (*ibid.*; Mees and Gutekunst, J. Ind. Eng. Chem. 1922, 14, 1061).

QUINOLINE-YELLOW.

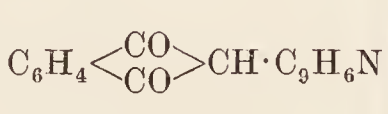
From quinaldine by condensation with phthalic anhydride in the presence of zinc chloride three products can be obtained, according to the temperature employed. To these have been assigned the structural formulæ :—



I (at 120°).



II (at 160°).



III (at 200°).

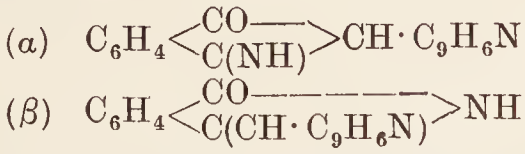
The substance represented by formula III is quinophthalone, which, when sulphonated by anhydrosulphuric acid in the cold, furnishes *quinoline-yellow*, a mixture of mono- and di-sulphonic acids, the sodium salt of which is a soluble yellow powder dyeing wool and silk a greenish-yellow fast to light and soap. Greater tinctorial power is shown by the condensation product of 6-chloroquinaldine and phthalic anhydride after conversion into sulphonic acid (Bayer, D. R.-P. 204255; Eng. P. 28266 of 1908), and greater fastness to light when the quinaldine contains in the 'benzene' nucleus both chlorine and a second substituent, usually methyl, one of which occupies the 8-position (Meister, Lucius & Brüning, D. R.-P. 286237; Eng. P. 8577 of 1914).

Quinophthalone (sym-*quinophthalone*; 2-*quinolylindandione*; formula III) can be prepared by heating quinaldine and phthalic anhydride in mol. prop. with zinc chloride at 200° (Jacobsen and Reimer, Ber. 1883, 16, 1082, 2602; *cf.* Traube, *ibid.* 298); or, quantitatively, by heating quinaldine with ethyl phthalate and sodium at 100° (Eibner and Lange, Annalen, 1901, 315, 346); *or* by heating *iso*quinophthalone (formula II) at 240°–250° or with benzaldehyde or sodium ethoxide (Eibner and Merkel, Ber. 1902, 35, 2298; 1904, 37, 3008); *or* by warming the compound I with caustic soda solution (Eibner and Lange, *l.c.*).

Preparation.—A mixture of quinaldine (5 pts.) and phthalic anhydride (6 pts.) is fused with zinc chloride (6 pts.) at 200°–210° for 5–6 hours; the melt boiled with dilute hydrochloric acid to extract zinc chloride, phthalic acid and unattacked base; and the insoluble residue filtered, ground, and dried (Jacobsen and Reimer, D. R.-P. 23188; 25144; Eng. P. 1362 of 1883). The product contains *iso* quinophthalone in amount which, depending on the temperature employed, may reach 25 p.c., but this can be transformed into quinophthalone by heating the melt with alcoholic sodium ethoxide until a uniform red mass is obtained. After filtration, the residue is boiled with water to decompose the sodium salt and then dried (Eibner, D. R.-P. 158761; Eibner and Merkel, Ber. 1904, 37, 3008).

Properties.—Quinophthalone crystallises in golden-yellow needles, m.p. 240°, is insoluble in water, sparingly soluble in boiling alcohol, but readily soluble in acetic acid and chloroform, and dyes wool and silk yellow. Its *monosodium* and *potassium* derivatives, which form orange-red needles, are hydrolysed by water regenerating the quinophthalone (Eibner and Merkel, Ber. 1904, 37, 3007).

Reactions.—When heated with hydrochloric acid at 240°, or fused with caustic alkali, it is resolved into *quinaldine* and *phthalic acid.* By digestion with alcoholic ammonia at 200° for 40 hours it is converted into *α-quinophthalin*, a basic yellow colouring matter (Meister, Lucius & Brüning, D. R.-P. 27785), forming garnet-red leaflets, m.p. 305° (Eibner and Hofmann, Ber. 1904, 37, 3021), isomeric with *β-quinophthalin*, pale yellow prisms,



m.p. 213°, obtained by adding phthalimide to a mixture of quinaldine and zinc chloride at 160°–180° (Eibner and Lange, *l.c.*; Eibner and Hofmann, *l.c.*).

*iso***Quinophthalone** (unsym-*quinophthalone*, 2-*quinaldylene-phthalide*; Formula II), formed when the quinophthalone reaction is carried out at a temperature not exceeding 160°, crystallises in orange-yellow prisms, m.p. 186°, dissolves only sparingly in alcohol but easily in

and dicyanines are also produced by the condensation of quinaldinium with lepidinium ethiodides, being characterised by strong absorption in the red end of the spectrum (*ibid.* 208). Dicyanine A has been obtained with a sensitising action extending to λ9000 (Mikeska, Haller and Adams, J. Amer. Chem. Soc. 1920, 42, 2393).

chloroform, and when heated at 240°–250°, or with benzaldehyde or with sodium ethoxide, is converted into *quinophthalone*. On digestion with alcoholic ammonia at 100°, it furnishes *quinaldine* and *phthalamide*; and with anhydrosulphuric acid at 100°, it forms quinoline-yellow (Eibner and Merkel, Ber. 1902, 35, 2297; *cf.* 1904, 37, 3008).

Homologues of both *sym-* and *unsym-*quinophthalone have been prepared, and these increase in fastness to light, covering power, and insolubility in alcohol with increase in molecular weight (Eibner and Hofmann, Ber. 1904, 37, 3017; Eibner, D. R.-P. 158761).

By the substitution of β-thiophthalic acid for phthalic anhydride in these condensations, compounds are obtained which dye unmordanted cotton in yellow shades, and on oxidation by the air or with dichromate give very fast colours (Gesellsch. chem. Ind. D.R.-P. 189943; Eng. P. 4159 of 1907).

***iso*QUINOLINE.** This base constitutes less than 1 p.c. of coal-tar quinoline, and can be isolated from this source by taking advantage of the fact that the acid sulphates of quinoline and quinaldine are more soluble in alcohol than the *iso*quinoline salt (Hoogewerff and van Dorp, Rec. trav. chim. 1885, 4, 125, 285; 1886, 5, 305; *cf.* Dewar, Roy. Soc. Proc. 1880, 30, 167). It is a much stronger base than quinoline, a difference utilised in effecting its separation by fractional conversion into the acid sulphate (Weissgerber, Ber. 1914, 47, 3176; Ges. f. Teerverw. D. R.-P. 285666), and by fractional liberation of the base from the acid sulphate (Harris and Pope, Chem. Soc. Trans. 1922, 121, 1030).

Isolation.—Harris and Pope achieve the separation of pure *iso*quinoline from coal-tar quinoline by shaking the fraction, b.p. 230°–255° (387 grs.) vigorously with 4*N*-sulphuric acid (600 c.c.), removing the undissolved base (20 p.c. of the whole) by shaking with a little benzene, adding sufficient 4*N*-ammonia solution (120 c.c.) to liberate 20 p.c. of the contained base, removing it by extraction with benzene and repeating these operations some eleven times until only about 7 p.c. (26·7 gr.) of the base originally used remains in solution. This is liberated by ammonia, and, after extraction, is dissolved in twice its weight of rectified spirit, converted into acid sulphate by the addition, with constant stirring below 30°, of the calculated amount of concentrated acid, and the crystalline separation recrystallised several times from 8–9 pts. of boiling alcohol until the m.p. rises to 206·5°. The base recovered from the pure salt boils sharply at 242·5° under 760 mm., the yield amounting to 1·5 p.c. of the weight of the fraction used.

Syntheses.—Two methods devised, one for the synthesis of *iso*quinoline and the other for that of certain of its derivatives, may be mentioned here, the first because it serves to throw light on the constitution of *iso*quinoline, and the second to illustrate the connexion between this base and the alkaloids.

When homophthalimide is heated with phosphorus pentachloride, and the dichloro*iso*quinoline thus formed reduced by hydriodic acid and phosphorus—

$$C_6H_4\langle\begin{matrix}CH_2\cdot CO\\CO\cdot NH\end{matrix}\rangle \rightarrow C_6H_4\langle\begin{matrix}CH:CCl\\CCl:N-\end{matrix}\rangle \rightarrow C_6H_4\langle\begin{matrix}CH:CH\\CH:N-\end{matrix}\rangle$$

*iso*quinoline is obtained (Gabriel, Ber. 1886, 19, 1655, 2361).

Derivatives of 3 : 4-dihydro*iso*quinoline, convertible by oxidation with acid permanganate into the corresponding *iso*quinoline compounds, are produced by heating acyl derivatives of ω-phenylethylamine with zinc chloride or phosphoric oxide (Bischler and Napieralski, Ber. 1893, 26, 1903), *or* by boiling their solutions in benzene, toluene, or xylene with phosphoric oxide (Pictet and Kay, Ber. 1909, 42, 1973), *or* by condensing the imino- chlorides (prepared from the acyl derivatives by interaction with phosphorus pentachloride) by the aid of aluminium chloride (Decker and Kropp, Ber. 1909, 42, 2075). This reaction has been applied to the synthesis of the alkaloids, laudanosine (Pictet and Finkelstein, Ber. 1909, 42, 1979), cotarnine (Salway, Chem. Soc. Trans. 1910, 97, 1209), and papaverine (Pictet and Gams, Ber. 1909, 42, 2943).

Preparation.—Benzylideneaminoacetal (1 pt.) obtained in good yield by mixing benzaldehyde and aminoacetal in mol. prop., is added carefully with constant cooling to sulphuric acid (2 pts.), and the solution allowed to mix slowly with sulphuric acid (3 pts.) maintained at 160°–170°. The product, diluted with water, is freed from benzaldehyde by steam, then rendered alkaline and *iso*quinoline removed by distillation with steam. The yield of pure base amounts to about 50 p.c. of that calculated (Pomeranz, Monatsh. 1893, 14, 118; Meister, Lucius & Brüning, D. R.-P. 80044; *cf.* Fischer, Ber. 1893, 26, 764; Staub, Helv. Chim. Acta, 1922, 5, 888; and for derivatives, Pomeranz, Monatsh. 1894, 15, 304; Fritsch, Annalen, 1895, 286, 1; D. R.-P. 85556; 86561).

Constitution.—When *iso*quinoline is oxidised by potassium permanganate in alkaline solution, it yields both *phthalic acid* and *cinchomeronic* (pyridine-3 : 4-dicarboxylic) *acid* (Hoogewerff and van Dorp, Rec. trav. chim. 1885, 4, 285), but in neutral solution it furnishes *phthalimide* (Goldschmiedt, Monatsh. 1888, 9, 676). From these results, coupled with those obtained by synthetical processes, the formula at the head of this section has been deduced for the base. The positions in the *iso*quinoline formula are numbered from 1 to 8, the nitrogen atom occupying the 2-position.

Properties.—*iso*Quinoline crystallises in tables, m.p. 24·6, b.p. 240·5° under 763 mm. (Hoogewerff and van Dorp), 242·5° (thread in vapour) under 760 mm. (Harris and Pope, Chem. Soc. Trans. 1922, 121, 1031), sp.gr. 1·0986 at 20°/4°, has an odour recalling those of benzaldehyde and of aniseed, being quite dissimilar to that of quinoline (Harris and Pope, *l.c.*), and is volatile with steam. It absorbs carbon dioxide from the air, and forms with acids a series of salts, the melting-points of which are higher than those of the corresponding quinoline

compounds. The *chromate*, $B_2 \cdot H_2Cr_2O_7$, forms needles, decomp. at 150°, the *picrate*, needles, m.p. 222°–223·5° (Pictet and Popovici, Ber. 1892, 25, 734); the *platinichloride*, $B_2 \cdot H_2PtCl_6 + 2H_2O$, needles, m.p. 263° (*ibid.*); the *methiodide*, $B \cdot CH_3I + H_2O$, yellow needles, m.p. 159° (Hoogewerff and van Dorp, *l.c.*). Unlike quinoline it does not give compounds with metallic salts. The *dibromide*, $B \cdot Br_2$, m.p. 82°, yields at 180°–200° a *bromo*isoquinoline, m.p. 40° (Edinger and Bossung, J. pr. Chem. 1891, [ii.] 43, 191); the *tetraiodide* forms dark blue crystals, m.p. 130° (Edinger, *ibid.* 1895, [ii.] 51, 205).

Reactions.—On reduction with tin and hydrochloric acid, or with sodium and boiling alcohol, it gives *tetrahydro*isoquinoline (Bamberger and Dieckmann, Ber. 1893, 26, 1209). By nitration with concentrated nitric acid it yields the 5- (or 8-) *nitro*isoquinoline, m.p. 110°, and, by further nitration, a *dinitro-* derivative (Fortner, Monatsh. 1893, 14, 146; Claus and Hoffmann, J. pr. Chem. 1893, [ii.] 47, 253). When sulphonated with 50–60 p.c. anhydrosulphuric acid, it gives a mixture of two *sulphonic acids*, which at 115° contains chiefly the α- (5- or 8- acid), and at 250°–260° chiefly the β- (probably the 6- or 7-) acid (Claus and Raps, J. pr. Chem. 1892, [ii.] 45, 242; Claus and Seelemann, *ibid.* 1895, [ii.] 52, 1). The α- acid is the less soluble and forms the less soluble barium salt; from it both a *cyano-* derivative (Jeiteles, Monatsh. 1894, 15, 807), and a *hydroxy-* derivative (Claus and Raps, *l.c.*) have been obtained.

When heated with quinaldine, benzotrichloride and zinc chloride at 120°, it yields iso*quinoline-red* (Hofmann, Ber. 1887, 20, 9).

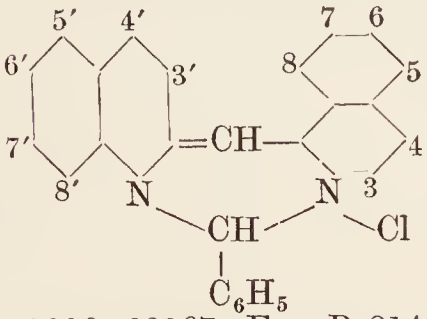
Physiological action.—As the physiological properties of *iso*quinoline and its derivatives proved to be identical with those of the much cheaper quinoline (Stockman, J. Physiol. 1894, 15, 245), little attention was given to the former until recently. The rapid progress of alkaloidal synthesis, however, has revived interest in the physiological study of *iso*quinoline, examples of which may be found in papers by Pyman (Chem. Soc. Trans. 1910, 97, 265), and Laidlaw (Bio-Chem. Journ. 1911, 5, 243).

Among its derivatives are the alkaloids papaverine (Goldschmiedt, Monatsh. 1885, 6, 667), narcotine (Roser, Annalen, 1889, 254, 357), laudanosine (Pictet and Finkelstein, Ber. 1909, 42, 1979), hydrastine (Freund and Rosenberg, Ber. 1890, 23, 414), and berberine (Perkin, Chem. Soc. Trans. 1890, 57, 1006).

Tetrahydro*iso*quinoline is formed when *iso*quinoline is reduced with tin and hydrochloric acid (Hoogewerff and van Dorp, Rec. trav. chim. 1886, 5, 310) or with sodium and boiling alcohol (Bamberger and Dieckmann, Ber. 1893, 26, 1209), or when a mixture of phenylethylamine and methylal is boiled with hydrochloric acid (Pictet and Spengler, Ber. 1911, 44, 2034; Pictet, D. R.-P. 241425).

Properties.—It is an oil, b.p. 232°–233°, absorbs carbon dioxide from the air, forms a *nitroso-* derivative, needles, m.p. 53°, an *acetyl* derivative, m.p. 46°, and in its properties shows much resemblance to benzylamine (Bamberger and Dieckmann, *l.c.*). The *hydrochloride*, $B \cdot HCl$, forms prisms, m.p. 195°–197°; the *platinichloride*, $B_2 \cdot H_2PtCl_6$, prisms, m.p. 231°–232°; and the *picrate*, needles, m.p. 195°. For the 2-alkyl derivatives, *cf.* Wedekind and Oechslen, Ber. 1901, 34, 2986.

***iso*Quinoline-red,** $C_{26}H_{19}N_2Cl$. This dye was obtained originally by heating benzotrichloride, benzochlorodibromide, or benzylidene chloride with a mixture of coal-tar quinoline and zinc chloride (Jacobsen, D. R.-P. 19306; 23967; Eng. P. 814 of 1882), and is formed by the interaction of benzotrichloride, *iso*quinoline and quinaldine in mol. prop., either at 150°, or more rapidly in the presence of zinc chloride at 120° (Hofmann, Ber. 1887, 20, 9). The quinaldine cannot be replaced by lepidine (Vongerichten and Homann, Ber. 1912, 45, 3447).



Preparation.—Harris and Pope find that with aluminium chloride as the condensing agent in place of zinc chloride, a 50 p.c. greater yield of dye is obtained and the product is freed much more easily from inorganic impurities. To a mixture of *iso*quinoline (5 gr.), quinaldine (5·2 gr.), and anhydrous aluminium chloride (2·5 gr.) heated at 90°, benzotrichloride (7·6 gr.) is added and the temperature then raised to 150°–155° for an hour. The melt, dissolved in a little dilute alcohol, is mixed with 10 p.c. milk of lime (1 litre), the mixture distilled with steam, the boiling solution (1·5 litres) filtered, the filtrate acidified with hydrochloric acid, and the dye, which separates on cooling, recrystallised from boiling water (380 c.c. for each gram of crystals), hydrochloric acid (1 c.c. to each 100 c.c. of solution) being added before crystallisation occurs (Chem. Soc. Trans. 1922, 121, 1032; *cf.* Vongerichten and Homann, *l.c.* 3449; Aktienges., D. R.-P. 40420).

Properties.—*iso*Quinoline-red forms dark red, bronze-lustred, monoclinic prisms, which dissolve only sparingly in cold water, but readily in hot water or alcohol; these solutions are carmine-red by transmitted light, and in reflected light show a marked yellowish-red fluorescence. When heated with hydrochloric acid or with alcoholic ammonium sulphide at 200° it yields *benzaldehyde* or *benzylmercaptan* respectively, and a *base* $C_{19}H_{14}N_2$, which crystallises in plates of golden lustre, m.p. 231° (Hofmann, *l.c.*; *cf.* Vongerichten and Homann, *l.c.*). By oxidation with potassium dichromate and sulphuric acid, it furnishes *benzaldehyde* and 2-*quinolyl*-1-iso*quinolyl ketone* (Vongerichten and Krantz, Ber. 1910, 43, 129; Vongerichten and Homann, *l.c.*). As a dye-stuff it is valueless, the rose-red shades on silk or wool not being fast to light; but, mixed with cyanine, it has been used in the preparation of orthochromatic ('azaline') plates for photographic purposes (Vogel, D. R.-P. 39779).

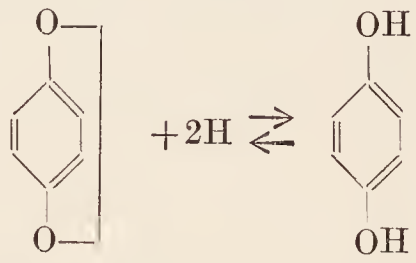
6′-Methyl- and 6′-ethyl-*iso*quinoline-red behave as photographic sensitisers in a manner almost identical with that of the parent substance, but are much less soluble in water (Harris and Pope, *l.c.*). W. P. W.

QUINOLINE DYES *v.* QUINOLINE.

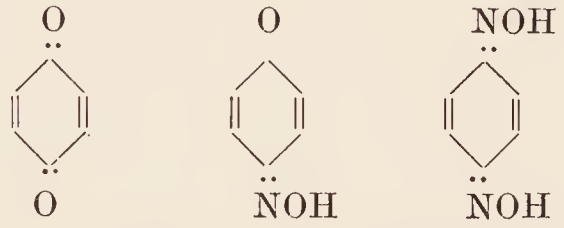
QUINOLINIC ACID *v.* BONE OIL.

QUINONE DIAZIDES (*cyclic diazo-oxides*) *v.* DIAZO COMPOUNDS.

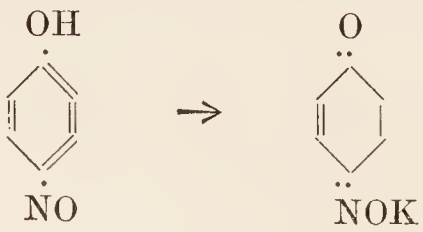
QUINONES are substances derived from aromatic hydrocarbons by replacement of two hydrogen by two oxygen atoms. The earliest known member of the series, *para*benzoquinone (or simply quinone) was obtained by the oxidation of various substituted benzenes (Woskresensky, Annalen, 1838, 27, 268; Wöhler, *ibid.* 1844, 51, 152); since it yields hexachlorobenzene when treated with phosphorus pentachloride, is easily reduced to *p*-dihydroxybenzene (quinol), and may be obtained from the latter by oxidising agents, the formula of a *p*-phenylene peroxide was assigned to it (Graebe, *ibid.* 1868, 146, 1). The relationship between quinone and quinol can then be represented by—



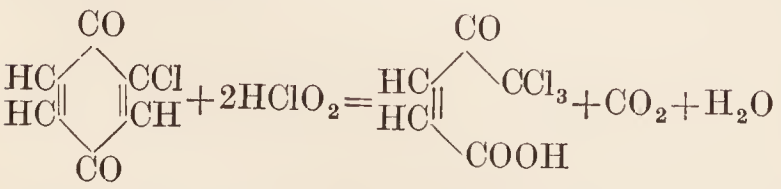
At a later date it was found that whilst quinone was reduced by free hydroxylamine, the hydrochloride gave an oxime which proved to be identical with *p*-nitrosophenol (Goldschmidt, Ber. 1884, 17, 805). The monoxime gave in turn a dioxime, these reactions pointing to the following respective formulæ for quinone, its mono- and its di- oximes.



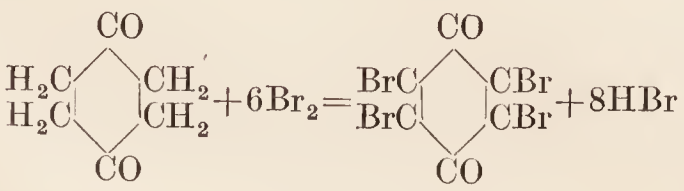
The constitution of quinone-oxime itself cannot be taken as absolutely settled; according to C. H. Sluiter (Rec. trav. chim. 1906, 25, 8), the free substance is *p*-nitrosophenol whilst the salts are derived from the quinone-oxime.



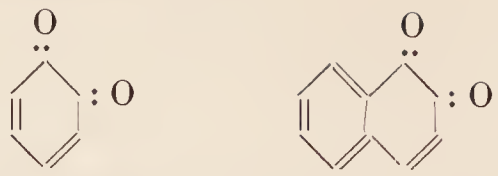
Additional support for the diketonic formula is afforded by the production of trichloroacetylacrylic acid when chlorous acid acts on benzene, quinone, &c. (Kekulé and Strecker, Annalen, 1884, 223, 170)—



and by the production of bromanil (tetrabromoquinone) from bromine and *cyclo*-hexane-1 : 4-dione



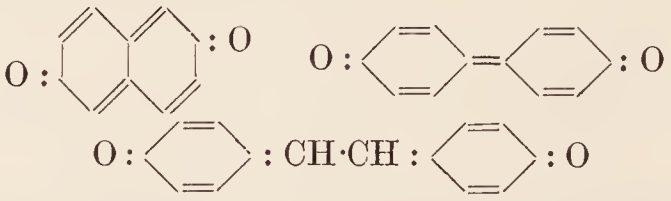
Ortho-quinones, *e.g.*



were discovered at a later date; metaquinones have not so far been obtained (R. Meyer and Desamari, Ber. 1908, 41, 2437; Zincke and Schwabe, *ibid.* 1909, 42, 797), it is doubtful whether they are capable of existence. The supposed tribromoresoquinone proved to be a bimolecular, keto-bromide (R. Meyer, Ber. 1913, 46, 1220) and the existence of metaquinonoid hydrocarbons also appears to be very doubtful. A case seemed to have been made out for tetraphenyl-*m*-xylylene (Stark and Garben, Ber. 1913, 46, 659, 2252, 2542) but a later paper by Stark and Klebahn (Ber. 1914, 47, 125) renders the results very doubtful.

The non-existence of internal meta-diazo-oxides is also of interest in this connection (Morgan and Tomkins, Chem. Soc. Trans. 1917, 111, 497).

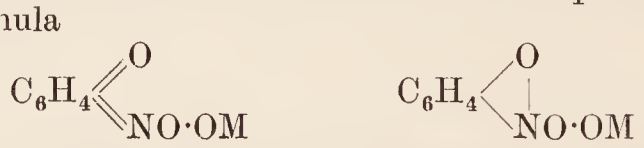
Within the last few years a number of quinonoid substances have been obtained by the oxidation of dihydroxyl derivatives of aromatic compounds in which the hydroxyl groups are attached to different nuclei; *amphi*-naphthaquinone, diphenoquinone and stilbene quinone may be cited as examples. In these cases the diketonic formulæ



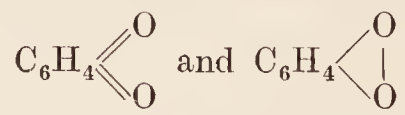
have the merit of simplicity when compared with the formulæ in which the two oxygen atoms are linked together.

Although the diketonic has been more popular than the peroxide formula during the past 25 years, the latter is showing a revival and cannot be disregarded.

The metallic salts of the nitrophenols may be written with a quinonoïd structure which has usually been derived from the diketonic formula. Hantzsch (Ber. 1907 40, 335) considers it at least necessary to take into account a quinonoïd structure derived from the peroxide formula



The discovery of two modifications of *o*-benzoquinone, one coloured and the other colourless, has led Willstätter and Müller (Ber. 1908, 41, 2580) to assign to them the respective formulæ

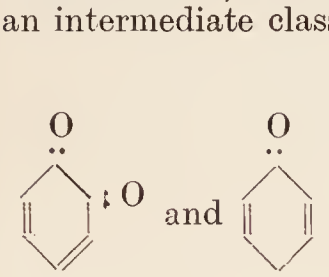


Kehrmann, however, advises caution, the colourless form has not been analysed and may be a hydrate, $O : C_6H_4 : (OH)_2$ (Ber. 1911, 44, 2632).

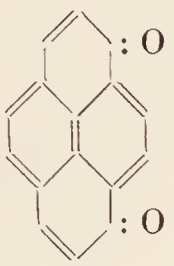
A comparison of the absorption spectra of *p*-benzoquinone and other aromatic compounds (Hartley and Leonard, Chem. Soc. Trans. 1909, 95, 34) leads Hartley to the conclusion that the

quinones must be considered as benzene derivatives (*ibid.* 58); and H. Haakh assumes that the feebly coloured *p*-benzoquinone has the peroxide constitution assigned to it by Graebe, the oxygen atoms having in this case no residual affinity. In the highly coloured additive compounds (with acids, salts, hydrocarbons, phenols, &c.), the quinone is supposed to acquire the diketonic constitution, addition occurring in virtue of the residual affinity of the oxygen atoms (J. pr. Chem. 1910, ii. 82, 546).

For purposes of classification, quinones will be regarded in this article as homonuclear and heteronuclear; a few will have to be placed in an intermediate class, *e.g.*



o- and *p*-Benzoquinones.



Pyrenequinone.



Diphenoquinone.

Occasionally the term ' quinone ' is applied to compounds containing two carbonyl groups in a five-membered ring (*e.g.* acenaphthenequinone), and several heterocyclic compounds containing two carbonyl groups (alloxan, isatin, &c.) exhibit many of the properties of quinones. Meanwhile hydroxypyridine quinone has been obtained by Peratoner and Tamburello (Gazz. chim. ital. 1911, 41, ii. 619).

Homonuclear Quinones.

General methods of preparation.

(1) By the oxidation of *o*- and *p*-dihydroxy-derivatives of aromatic hydrocarbons. 1 : 2 : 4-trihydroxy-compounds might give *o*- or *p*-quinones; the *p*-quinoid configuration is usually favoured, but 2-hydroxy-1 : 4-naphthaquinone and 4-hydroxy-1 : 2-naphthaquinone appear to be tautomeric.

(2) By the oxidation of aromatic hydrocarbons, their hydroxy-, amino-, *p*-hydroxyamino-derivatives, &c.

(3) By the acid hydrolysis of indophenols (the compounds resulting from the oxidation of mixtures of phenols and *p*-diamines).

$$C_6H_5OH+NH_2\cdot C_6H_4\cdot N(CH_3)_2+2O = 2H_2O+O:C_6H_4:N\cdot C_6H_4\cdot N(CH_3)_2$$

$$O:C_6H_4:N\cdot C_6H_4\cdot N(CH_3)_2+H_2O = O:C_6H_4:O+NH_2\cdot C_6H_4\cdot N(CH_3)_2$$

(Bayrac, Bull. Soc. chim. 1894, iii. 11, 1129).

(4) By warming diketones of the type $CH_3\cdot CO\cdot CO\cdot R$ with dilute sodium hydroxide

$$2CH_3\cdot CO\cdot CO\cdot CH_3=2H_2O+C_6H_2(CH_3)_2O_2$$

(von Pechmann, Ber. 1888, 21, 1417).

Properties and general reactions.

(1) The quinones are solid at ordinary temperatures, generally volatile with steam and are coloured.

(2) Easily reduced to dihydroxy-aromatic compounds. The latter, when cautiously oxidised, furnish quinhydrones as intermediate products; these may also be obtained by careful reduction of quinones.

(3) Quinones easily form additive compounds. Besides the quinhydrones, additive compounds may be obtained with aromatic hydrocarbons, bases, metallic salts, &c. (*see* below *Addition compounds of quinones*).

(4) Quinones react with many compounds RH to furnish R-substituted quinols

$$C_6H_4O_2+RH=C_6H_3R(OH)_2$$

In reactions of this kind

$$R=Cl,Br,\cdot SO_3K,C_6H_5\cdot SO_2,\ \&c.$$

Wöhler found that quinone and hydrogen chloride give chloroquinol (Annalen, 1844, 51, 155). Difficulty has been found in accepting Thiele's theory of the addition process (*ibid.* 1899, 306, 133), owing to the intermediate production of quinhydrone, first observed by Staedeler (*ibid.* 1849, 69, 308). Schmidlin has shown that this is no real objection and Thiele's theory may be accepted (Ber. 1911, 44, 1700; *see Addition compounds of quinones* for a discussion).

(5) Quinones are easily chlorinated and generally the chlorine may be partially replaced by hydroxyl.

(6) Ammonia and amines yield amino-substituted quinones, with simultaneous reduction of a portion of the quinone

$$3C_6H_4O_2+2C_6H_5NH_2 = C_6H_2(NHC_6H_5)_2O_2+2C_6H_4(OH)_2$$

Dry quinones do not absorb dry ammonia (Hantzsch and Dollfus, Ber. 1902, 35, 241).

Compounds of the types $C_6H_4(:NR):O$ and $C_6H_4(:NR)_2$ are obtained by indirect means; usually by oxidising amino-phenols, *p*-diamines and their derivatives. Compounds such as $O:C_6H_4:N\cdot C_6H_4\cdot NH_2$ and

$$NH:C_6H_4:N\cdot C_6H_4\cdot NH_2$$

(as well as their alkyl derivatives) are known as indophenols and indamines (*q.v.*) respectively.

(7) Free hydroxylamine reduces quinones to quinols; with hydroxylamine hydrochloride oximes are produced.

$$C_6H_4O_2 \rightarrow C_6H_4O(:NOH) \rightarrow C_6H_4(:NOH)_2$$

Quinone monoximes are also formed by the action of nitrous acid on phenols

$$C_6H_5OH+HO\cdot NO=H_2O+C_6H_4(OH)(NO)$$

or $$C_6H_4(:O)(:NOH)$$

The dioximes are oxidised to *p*-dinitroso or *p*-dinitro-derivatives of the hydrocarbons by potassium ferricyanide or fuming nitric acid respectively.

(8) The chloro-imines corresponding to the oximes are obtained by the action of chloride of lime solution on the hydrochlorides of the *p*-aminophenols and the *p*-diamines.

$$NH_2\cdot C_6H_4\cdot OH+2Cl_2=3HCl+ClN:C_6H_4:O$$

$$NH_2\cdot C_6H_4\cdot NH_2+3Cl_2=4HCl+ClN:C_6H_4:NCl$$

The monochloroimines react with tertiary amines giving indophenols.

$$C_6H_4O(:NCl)+C_6H_5\cdot NR_2 = HCl+O:C_6H_4:N\cdot C_6H_4\cdot NR_2$$

(9) By magnesium alkyl halides, pseudo-quinols, *e.g.* $O:C_6H_2(CH_3)_2<\begin{matrix}CH_3\\OH\end{matrix}$ are produced (Bamberger and Blangey, Ber. 1903, 36, 1625).

(10) Quinones react with one or two molecules of ketenes, the β-lactones obtained in this way lose carbon dioxide if heated under certain conditions, and quinomethanes or quinodimethanes are formed.

$$O{:}C_6H_4{<}\overset{C(C_6H_5)_2}{\underset{\text{———}O}{\text{}}}{>}CO = CO_2 + O{:}C_6H_4{:}C(C_6H_5)_2$$

$$CO{<}\overset{C(C_6H_5)_2}{O\text{———}}{>}C_6H_4{<}\overset{C(C_6H_5)_2}{\text{———}O}{>}CO$$
$$= 2CO_2 + (C_6H_5)_2C : C_6H_4 : C(C_6H_5)_2$$

Under other conditions, the mono-β-lactones undergo intramolecular rearrangement with production of γ-lactones

$$O : C_6H_4{<}\overset{C(C_6H_5)_2}{\underset{\text{———}O}{\text{}}}{>}CO$$
$$= HO{\cdot}C_6H_3{<}\overset{C(C_6H_5)_2}{\underset{\text{———}O}{\text{}}}{>}CO$$

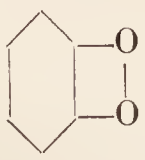
(Staudinger and Bereza, Annalen, 1911, 380, 243).

Quinones $C_nH_{2n-8}O_2$.

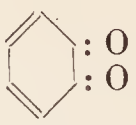
***o*-Benzoquinone** $C_6H_4O_2$ is obtained in chloroform solution by the action of iodine on the lead derivative of catechol (Jackson and Koch, Amer. Chem. J. 1901, 26, 21), and can be isolated in a solid condition when catechol dissolved in an indifferent solvent (*e.g.* dry ether) is treated with silver oxide (Willstätter and Müller, Ber. 1908, 41, 2580). Working rapidly with small quantities of materials, the compound may be obtained as colourless prisms; working more slowly a stabler, bright red form is obtained.

The colourless modification either changes into the red form on keeping or decomposes. It frequently explodes when rubbed, liberates iodine immediately from acidified potassium iodide, turns guaiacum tincture blue, and oxidises hydrocoerulignone. It is reduced by sulphurous acid to catechol.

The red modification is more soluble in ether; it is formed by spontaneous transformation of the colourless variety. There is apparently an equilibrium between the two modifications, as a small amount of the colourless variety is usually produced when the red modification is recrystallised. According to Willstätter and Müller, the two forms may be represented structurally thus:—



Colourless.



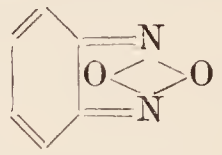
Red.

Several papers dealing with the peroxide formula for *o*-quinones have appeared (*see* Schönberg, Ber. 1922, **55**, 3746, 3753). Kehrmann suggested that the colourless modification is a hydrate (Ber. 1911, 44, 2632). Subsequently (Ber. 1913, 46, 3009) he considered the two forms to be dimorphous, stating further that the modification previously described as colourless is really green. If catechol is oxidised in acetic acid in presence of aniline 4 : 5-dianilino-1 : 2-benzoquinone, m.p. 193°, is produced.

Diimine $C_6H_4(NH)_2$. Known only in solution. After adding acid, diaminophenazine and 2 : 2′-diaminoazobenzene may be isolated (Willstätter and Pfannenstiehl, Ber. 1905, 38, 2348).

Monoxime $C_6H_4O(:NOH)$. Obtained as an oil by the hydrolysis of *o*-nitrosoanisole (Baeyer and Knorr, *ibid.* 1902, 35, 3037; see also, Baudisch and Karzeff, *ibid.* 1912, 45, 1164).

Dioxime $C_6H_4(:NOH)_2$, m.p. 145° (Green and Rowe). By the action of hydroxylamine on so-called *o*-dinitrosobenzene (Zincke and Schwarz, Annalen, 1899, 307, 39). The various substances which have been described as dinitroso-compounds probably possess a different constitution. Forster and Fierz suggested the constitution of quinone-dioxime peroxides (Chem. Soc. Trans. 1907, 91, 1942) whilst Green and Rowe (*ibid.* 1912, 101, 2452) regarded them as furoxans or furazan oxides, obtaining the so-called dinitrosobenzene by oxidation of alkaline solution of *o*-nitraniline with hypochlorite. Green and Rowe (Chem. Soc. Trans. 1913, 103, 897) and Forster and Barker (*ibid.* p. 1918) agreed eventually that the constitution was best represented by—



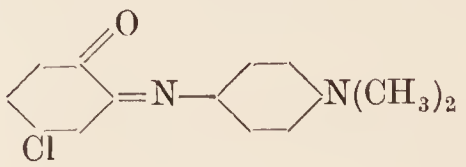
(See further Green and Rowe, Chem. Soc. Trans. 1913, 103, 2023; 1917, 111, 612). It is noteworthy that 8-nitro-1-naphthylamine gives no compound of this type (F. & F.; G. & R.). Gives phenylenefurazane $C_6H_4{\ll}\overset{N}{\underset{N}{}}{>}O$ when boiled with acetic anhydride.

o-Benzoquinone and α-benzoylphenylhydrazine give *o*-benzoxyazobenzene (m.p. 93°), and not the isomeric quinonehydrazone (McPherson and Lucas, J. Amer. Chem. Soc. 1909, 31, 281).

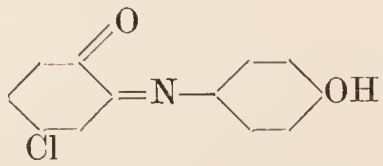
3-Chloro-*o*-benzoquinone $C_6H_3ClO_2$. By oxidation of 3-chlorocatechol with lead peroxide in suspension in ether and petroleum ether. Red crystals, discolours at 63°, decomposes at 68° (Willstätter and H. E. Müller, Ber. 1911, 44, 2189).

4-Chloro-*o*-benzoquinone. From 4-chlorocatechol dissolved in ether with silver oxide. Red crystals, m.p. 78° (Willstätter and Müller).

The only indophenols of the ortho- series which have been described, are derivatives of this quinone. Even in this case it is doubtful whether the chlorine atom has not been displaced and the indophenols obtained do not really belong to the *para* series (Friedländer, Fortschritte der Theerfarben-fabrikation, viii. 494). Attempts at preparing indophenols, using *p*-cresol and phenol-*p*-sulphonic acid, have been without result, but indophenols are formed when *p*-chlorophenol is oxidised along with a *p*-diamine or a *p*-aminophenol. To the resulting compounds, structures such as



and



have been assigned (Meister, Lucius and Brüning, D. R. P. 158091, 1903).

A solution of dimethyl-*p*-phenylene diamine in 15,000 parts of water prepared from 150 parts of nitrosodimethylaniline, 86 parts of concentrated hydrochloric acid, and 186 parts

of zinc dust is mixed with 140 parts of crystallised *p*-chlorophenol, 120 parts of soda-lye, and 212 parts of sodium carbonate in 12,000 parts of water. 1318 parts of potassium ferricyanide in 3500 parts of water are then run in and the indophenol separates out at once. It dissolves in alcohol with a blue colour, which becomes redder in shade on addition of acids. It dissolves easily in sodium sulphide solution as the leuco- compound. In place of ferricyanide, hypochlorites may be used for the oxidation.

Both the indophenol and its leuco- compound, when heated with alkaline polysulphides, give a blue colouring matter ; addition of copper at the same time causes the formation of a green dye.

To prepare the hydroxyindophenol, 11 parts of *p*-aminophenol, 60 parts of water, and 10 parts of 40 p.c. hydrochloric acid are mixed with 13 parts of *p*-chlorophenol and 33 parts of caustic soda-lye of 40°Bé. in 100 parts of water. This mixture is run into a second mixture made from 290 parts of sodium hypochlorite solution (containing 49 grams of active chlorine per kilogram), 200 parts of sodium chloride, and 200 parts of ice. The sodium salt of the oxidation product separates as a green crystalline mass. The aqueous solution is reddened by acetic acid ; concentrated sulphuric acid gives a deep blue solution.

4 : 5-**Dichloro-*o*-quinone** $C_6H_2Cl_2O_2$, m.p. 94°. By oxidising 4 : 5-dichloro-catechol dissolved in ether with silver oxide (Willstätter and Müller).

Tetrachloro-*o*-quinone $C_6Cl_4O_2$, m.p. 129°–130°. By oxidation of tetrachlorocatechol with nitric acid, or by the action of chlorine on catechol dissolved in hot acetic acid (Zincke, Ber. 1887, 20, 1779 ; 1888, 21, 2730 ; Cousin, Compt. rend. 1899, 129, 967 ; Jackson and MacLaurin, Ber. 1905, 38, 4103).

Tetrabromo-*o*-quinone $C_6Br_4O_2$, m.p. 150°–151°. By oxidation of tetrabromocatechol with bromine (Stenhouse, Annalen, 1875, 177, 197), chlorine or nitric acid (Zincke, Ber. 1887, 20, 1777). Thick dark red prisms or tablets. Acts as an oxidising agent. Yields dibromo-dianilino-*o*-quinone, m.p. 160°, when treated with aniline (Jackson and Porter, *ibid.* 1902, 35, 3851). Sodium hydroxide gives tetrabromocatechol and a *cyclo*-pentadiene derivative (Jackson and Fiske, *ibid.* 1909, 42, 2636). For other reactions, *see* Cousin (*l.c.*) and Jackson and Russe (Ber. 1905, 38, 419 ; Amer. Chem. J. 1906, 35, 154) ; Jackson and Beggs (J. Amer. Chem. Soc. 1916, 38, 676).

3-**Hydroxy-*o*-benzoquinone** $C_6H_3(OH)O_2$, m.p. 206°–208°. Colourless prismatic needles by acting on an alcoholic solution of pyrogallol with amyl nitrite and acetic acid. *Acetyl derivative*, m.p. 273° (A. G. Perkin and Steven, Chem. Soc. Trans. 1906, 89, 803).

3-**Methoxy-*o*-benzoquinone** $C_6H_3(OCH_3)O_2$. Dark red crystals, m.p. 115°–120° (Willstätter and F. Müller, 1911, 44, 2179).

3-**Methoxy-4-chloro-*o*-benzoquinone.** The dioxime is known (Green and Rowe, Chem. Soc. Trans. 1912, 101, 2452).

3 : 5 : 6-**Trichloro-4-methoxy-*o*-benzoquinone** $C_6Cl_3(OCH_3)O_2$, m.p. 93°–94°. By oxidation of 3 : 5 : 6-trichloro-2 : 4-dimethoxyphenol. Hydrolysed to trichlorohydroxy-*p*-benzoquinone (Zincke and Schaum, Ber. 1894,, 27 555).

p-**Benzoquinone** (*quinone*), $C_6H_4O_2$. Obtained by the action of chromic acid mixture on quinic acid (Woskresensky, Annalen, 1838, 27, 268), quinol (Wöhler, *ibid.* 1844, 51, 152), aniline, benzidine (Hofmann, Jahresb. 1863, 415), *p*-phenylenediamine (*ibid.* 422), sulphanilic acid (Meyer and Ador, Annalen, 1871, 159, 7 ; Schrader, Ber. 1875, 8, 760), phenol-*p*-sulphonic acid (Schrader), arbutin (Strecker, Annalen, 1858, 107, 233), various plant constituents (Stenhouse, *ibid.* 1854, 89, 247), aniline black (Nietzki, Ber. 1877, 10, 1934). By decomposition of the compound $C_6H_4(CrO_2Cl)_2$ with water (Etard, Ann. Chim. 1881, v. 22, 270), by hydrolysis of certain indophenols (*v. supra*), by the fermentation of fresh grass (Emmerling, Ber. 1897, 30, 1870), by oxidation of betite, $C_6H_{12}O_4$ (v. Lippmann, *ibid.* 1901, 34, 1162), by the action of iodine on the lead derivative of quinol (Jackson and Koch, *ibid.* 1898, 31, 1458 ; Amer. Chem. J. 1901, 26, 20) and by the electrolytic oxidation of aniline or benzene in acid solution salts of chromium, manganese, or vanadium being present.

Bamberger and Tschirner indicate that phenylhydroxylamine and *p*-aminophenol are intermediate products in the oxidation of aniline to quinone (Ber. 1898, 31, 1524). The theory of the formation of quinone from aniline is also dealt with by Willstätter and Dorogi (*ibid.* 1909, 42, 2147).

Preparation of *p*-Benzoquinone.

(*a*) By oxidation of aniline with chromic acid. According to Nietzki's directions (Ber. 1886, 19, 1468 ; *see* also Annalen, 1882, 215, 127), a concentrated solution of sodium dichromate is added to a well-cooled solution of 1 part of aniline in 25 parts of water and 8 parts of sulphuric acid. The quinone is subsequently extracted by ether. For modified methods of oxidising aniline, quinol, &c., see Seyda (Ber. 1883, 16, 687), Schniter (*ibid.* 1887, 20, 2283), Hesse (Annalen, 1880, 200, 240), Sarauw (*ibid.* 1881, 209, 99), Clark (Amer. Chem. J. 1892, 14, 555).

(*b*) By anodic oxidation of aniline in a cooled solution of chromium sulphate and sulphuric acid. The liquid is continually agitated during the process (F. Darmstädter, D. R. P. 109012, 1897).

(*c*) By anodic oxidation of aniline or quinol in sulphuric acid in presence of manganese sulphate. The outer cathode cell contains 20 p.c. sulphuric acid, a lead electrode and a porous earthenware vessel which serves as the anode cell ; as anode a lead cylinder is used. A mixture of 25 parts by weight of manganese sulphate, 100 parts by weight of water and 10 parts by weight of concentrated sulphuric acid are placed in the anode cell, the whole apparatus thoroughly cooled and a current of 175 ampères per square metre passed until about half of the manganese sulphate is oxidised : care is necessary to prevent the temperature rising above 0° in the anode cell. A well-cooled solution of 20 parts by weight of aniline in 300 parts by weight of water and 160 parts by weight of concentrated sulphuric acid is then added to the contents of the anode cell, which is well stirred and the current passed until all the aniline black is oxidised. In making quinone from quinol, 30 parts by weight of the latter in 300 of water and 160 of concentrated sulphuric acid are added and the current passed until the

dark green quinhydrone disappears (C. F. Boehringer und Söhne, D. R. P. 117129, 1899).

(*d*) By anodic oxidation of aniline in presence of vanadic acid. A quantitative employment of the anodic oxygen is claimed when sulphuric acid of 10 p.c. strength to which 3 p.c. of vanadic acid (calculated on the sulphuric acid) has been added. The temperature is kept at 5°–10°; E.M.F., 3–4 volts; current density, 400 ampères per square metre. For a good yield it is well to add the aniline in small quantities (Meister, Lucius and Brüning, D. R. P. 172654, 1903).

(*e*) Preparation of *p*-benzoquinone and quinol by the electrolytic oxidation of benzene. Benzene when emulsified with dilute sulphuric acid is oxidised to quinone by lead peroxide; on the other hand quinone may be reduced to quinol cathodically. Since lead peroxide is produced on a lead anode the two operations may be combined if a cell with a diaphragm is used. A lead disc which has been coated mechanically or electrically with peroxide serves as the anode and is rapidly rotated in a narrow glass cell, the anode space containing 150 c.c. of 10 p.c. sulphuric acid and 90 c.c. of benzene. The current is about 1 ampère per square decimetre, E.M.F. 4 volts. The quinone, as produced, dissolves in the excess of benzene. If the mixture of dilute acid and benzene solution of quinone be then transferred to the cathode cell, the quinone is reduced to quinol which passes into the dilute sulphuric acid. It may be extracted from the solution with ether, whilst the excess of benzene may be returned to the anode cell (Kempf, D. R. P. 117251, 1899; Zeitsch. Electrochem. 1901, 7, 592; J. pr. Chem. 1911, ii. 83, 329).

(*f*) By subjecting benzene vapour to the action of a gas containing oxygen at a suitable temperature and in the presence of a catalyst (Weiss and Downs, U.S. Pat. 1318631). Pumice impregnated with vanadium oxide may be employed at 300°–700°, but compounds of other metals may be used. Maleic acid which is formed as a by-product can be removed by solution in water.

p-Benzoquinone forms long, yellow, monoclinic prisms. It sublimes in gold-coloured needles; the odour is penetrating and reminiscent of the halogens. Slightly soluble in cold, easily in hot water, as also in alcohol and ether; fairly soluble in boiling petroleum spirit: m.p. 115·7°; sp.gr. 1·307–1·318; molecular heat of combustion at constant pressure, 658·4 cal. (Valeur, Ann. Chim. 1900, vii. 21, 475; Berthelot and Recoura found 656·8 cal., *ibid.* 1888, vi. 13, 312; *see* also Compt. rend. 1897, 125, 872).

Quinone dissolves in cold concentrated nitric acid without change; on heating, oxalic acid is formed (Schoonbroodt, Bull. Soc. chim. 1861, i. 3, 107; Sertini, Gazz. chim. ital. 1902, 32, i. 322). Heated by itself to 160°, or with water in a sealed tube to 100°, quinol and quinhydrone are formed (Scheid, Annalen, 1883, 218, 227; *see* also action of aqueous sodium acetate; Hesse, *ibid.* 1883, 220, 367). Electrolytic reduction of quinone to quinhydrone (Law, Chem. Soc. Trans. 1912, 101, 1551). Quinone, especially when exposed to light (Ciamician, Gazz. chim. ital. 1886, 16, 111; Ciamician and Silber, Rendiconti d. R. Accad. d. Lincei, 1901 [v.] 10, i. 93) acts as an oxidising agent. An alkaline solution of quinone, however, absorbs oxygen from the air.

When mixed with benzene as vapour and treated with a gas containing oxygen under pressure at 300°–700° in presence of vanadium oxide, maleic acid is produced (Weiss and Downs, U.S. Pat. 1318632).

Quinone gives addition products with one or two molecules of chlorine or bromine (Clark, Amer. Chem. J. 1892, 14, 357, 556; Peratoner and Genco, Gazz. chim. ital. 1894, 24, ii. 384; Sarauw, Annalen, 1881, 209, 111; Nef, J. pr. Chem. 1890, ii. 42, 182), and with metallic chlorides, *e.g.* $C_6H_4O_2 \cdot SnCl_4 \cdot C_6H_6$ (K. H. Meyer, Ber. 1908, 41, 2568). The addition products with phenols, &c., are dealt with under a separate heading.

Reduction by sodium sulphite gives sodium quinolsulphonate as chief product (Pinnow, J. pr. Chem. 1914, [ii] 89, 536; Dodgson, Chem. Soc. Trans. 1914, 105, 2435).

Hydrogen chloride is added with formation of chloroquinol; the action of hydrogen bromide is somewhat similar. Various compounds are produced by the action of phosphorus trichloride and phosphoryl chloride (Scheid, Annalen, 1883, 218, 198). Quinone and ammonia gas give 'quinone amide,' $3C_6H_4O_2 \cdot NH_3$ (?) (Woskresensky, Berz. Jahresbericht, 26, 801). The action of ammonia in presence of solvents has been studied by Knapp and Schultz (Annalen, 1881, 210, 178) and by Hebebrand and Zincke (Ber. 1883, 16, 1556). Carbamide at 150° gives a monoureïde to which the constitution

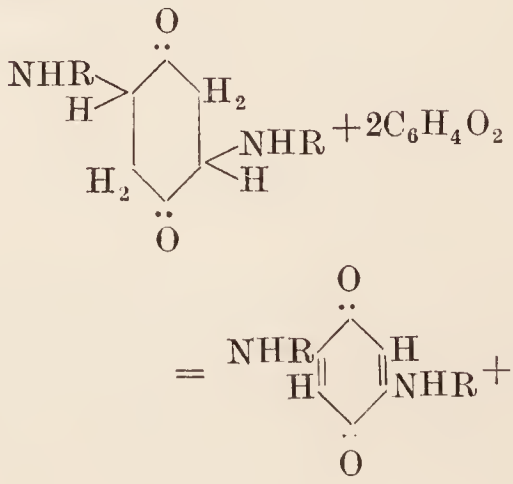
$$O : C_6H_4 \begin{matrix} NH \\ NH \end{matrix} > CO$$

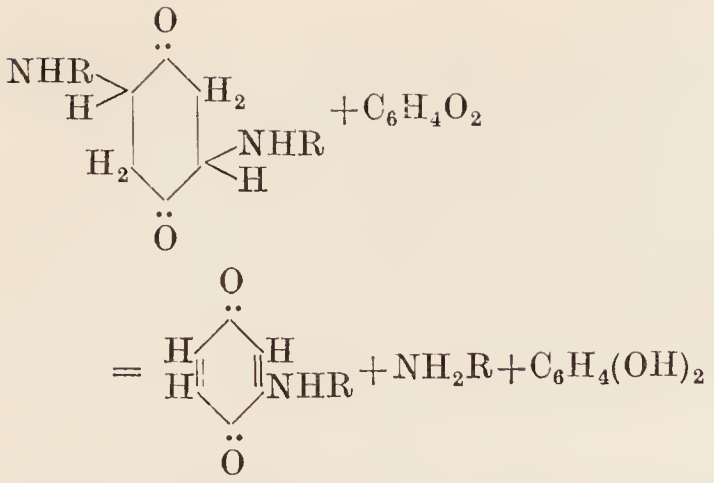
has been assigned (Grimaldi, Gazz. chim. ital. 1895, 25, i. 79; 1897, 27, i. 240).

A product of m.p. 234° is obtained by heating with isoprene. This seems to be a hydrogenised dimethylanthraquinone (Euler and Josephson, Ber. 1920, 53, 822).

Quinone reacts with many compounds containing the amino-group, *e.g.* anthranilic acid, *o*-nitroaniline (Hebebrand, Ber. 1882, 15, 1976; Leicester, Chem. News, 1896, 74, 236), *p*-nitroaniline (Hebebrand), diamino-diphenylmethane, piperidine (Schmidt and Sigwart, Ber. 1913, 46, 1491), benzidine (Brass, Ber. 1913, 46, 2902), &c. Naphthylamine-sulphonic acids condense in presence of sodium acetate, giving products useful in the manufacture of dyestuffs (Meister, Lucius and Brüning, D. R. P. 257834).

Suchanek (J. pr. Chem. 1914, [ii] 90, 467) considers that the formation of anilino-quinones takes place in two stages, an addition product of quinone and two molecules of primary base being first formed, which is then oxidised by the excess of quinone—



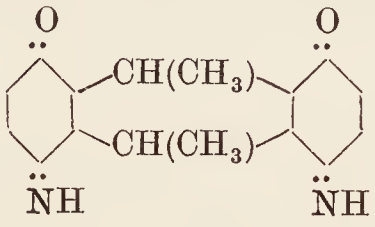


H. Suida and W. Suida (Annalen, 1918, 416, 113) consider this view of the formation of anilino-quinones incorrect, as in some cases the reaction may be observed to pass through the monoanilide stage. The reaction appears to depend in some way on the benzene nucleus, since open chain compounds with the grouping ·CO·CH : CH·CO· (*e.g.* maleic and fumaric esters and *cis*- and *trans*-dibenzoylethylene) do not react in this manner with aromatic amines (see also Meyer and Suida, *ibid.* p. 181, and Trutscher, *ibid.* p. 189 ; Siegmund, J. pr. Chem. 1910, ii. 82, 409). Free hydroxylamine acts as a reducing agent ; the hydrochloride yields either the mono- or the di-oxime. Phenylhydrazine and $\alpha\alpha$-phenylbenzylhydrazine are oxidised by quinone, but $\alpha\alpha$-phenylbenzoylhydrazine yields a hydrazone $(C_6H_5)(C_7H_5O)N{\cdot}N : C_6H_4 : O$, which gives benzeneazophenol on hydrolysis. The compound is, however, isomeric with the ester obtained by the direct benzoylation of the azophenol (McPherson, Ber. 1895, 28, 2415 ; Amer. Chem. J. 1899, 22, 366, 377). Quinone and its monoxime condense normally with hydrazides of the type $R{\cdot}CO{\cdot}NH{\cdot}NH_2$ (Borsche, Annalen, 1905, 343, 176), as well as with 2 : 4 : 6-trinitrophenylhydrazine (Borsche, Ber. 1921, 54, 1287). The resulting trinitrobenzeneazophenol is readily decomposed into phenol, nitrogen, and picric acid by cold, dilute alkalies.

Anhydrous hydrogen cyanide is without action on quinone (Levy and Schultz, Annalen, 1881, 210, 143), but the nascent acid gives 2 : 3-dicyanoquinol (Thiele and Meisenheimer, Ber. 1900, 33, 675 ; Bayer and Co., D. R. P. 117005, 1899).

Diazomethane gives a compound from which 1 : 4-diketobenzo*bis*-dihydropyrazole can be obtained (v. Pechmann and Seel, Ber. 1899, 32, 2295). Azoimide gives quinhydrone and 2-azidoquinol (Oliveri-Mandalà and Calderaro, Gazz. chim. ital. 1915, 45, i. 307). Phenylazoimide reacts with quinone yielding quinhydrone, 4 : 7-diketo-1-phenyl-1 : 2 : 3-benztriazole (m.p. 180°–184°), 4 : 8-diketo-1 : 5-diphenylbenzditriazole (decomposes about 340°), 4 : 8-diketo-1 : 7-diphenylbenzditriazole (m.p. 280°–285°), and a yellow substance, $C_{18}H_{14}O_2N_4$ (m.p. 157°), of unknown constitution (Wolff and Grau, Annalen, 1912, 394, 68). 2-Methylindole condenses forming a carbon linkage, the product, 2-methylindyl-3-benzoquinone forms dark violet bronze needles, m.p. about 185° (Möhlau and Redlich, Ber. 1911, 44, 3605). In presence of zinc chloride, primary alcohols give 2 : 5-dialkyl-1 : 4-quinones (Knoevenagel and Bückel, *ibid.* 1901, 34, 3993) ; with resorcinol in acetic acid solution, 1 : 4 : 3′-trihydroxydiphenyl ether is produced on addition of a few drops of dilute sulphuric acid : α-naphthol gives a similar reaction (Friedländer and Blumenfeld, *ibid.* 1897, 30, 1464, 2568 ; D. R. P. 96565, 1897). Boiled with anthranol in nitrobenzene solution, a compound, $C_{20}H_{10}O_3$ (black powder), is produced (Meister, Lucius and Brüning, D. R. P. 251020, 1911). The products obtained from anthranil and quinones are said to be used as vat-dyestuffs. Benzhydrol condenses with quinone in a mixture of acetic and sulphuric acids to benzoquinone-*bis*-diphenylmethane (Möhlau and Klopfer, Ber. 1899, 32, 2147). Möhlau regarded this reaction as characteristic of quinonoid compounds. Aromatic aminohydroxy acids gives quinoneimide mordant dyestuffs (v. Heyden, D. R. P. 119863, 1898).

Acetaldehyde unites with quinone on exposure to sunlight giving acetoquinol (Klinger and Kolvenbach, Ber. 1898, 31, 1214). Acetaldehyde ammonia gives a black compound, possibly



(Ghosh, Chem. Soc. Trans. 1917, 111, 608). With ethyl acetoacetate and zinc chloride, the ethyl esters of *p*-hydroxybenzo-α-methylfurane carboxylic acid, $C_{10}H_7O_4{\cdot}C_2H_5$, and benzo-dimethyl-*p*-difurane-dicarboxylic acid, $C_{14}H_8O_6(C_2H_5)_2$, are produced.

Buschka (Ber. 1881, 14, 1327) and Sarauw (Annalen, 1881, 209, 129) both obtained diacetylquinol from quinone and acetic anhydride, acetyl chloride gave the diacetyl derivatives of chloroquinol, dichloroquinol, and quinol (small amount). Thiele finds that acetic anhydride in presence of concentrated sulphuric acid gives 1 : 2 : 4-triacetoxybenzene (Ber. 1898, 31, 1247). To carry out this reaction technically, 15 kilos. of quinone are added gradually to a mixture of 40–45 kilos. of acetic anhydride and 1 kilo. of concentrated sulphuric acid. The mixture becomes hot and the quinone dissolves : the temperature should be kept at 40°–50°. When no further heat development is observed, the triacetoxybenzene is precipitated by pouring into water (Bayer and Co., D. R. P. 101607, 1897). A modified process is to add 10 kilos. of quinone to 30–40 kilos. of acetic anhydride in which 0·5 kilo. of crystallised phosphoric acid has been dissolved. Reaction takes place at the ordinary temperature and requires several days for completion (Bayer and Co., D. R. P. 107508, 1898).

Quinone and ‘ triphenylmethyl ’ give quinol-triphenylmethyl ether, $C_6H_4[O{\cdot}C(C_6H_5)_3]_2$; m.p. 241° (Schmidlin, Wohl and Thommen, Ber. 1910, 43, 1298).

The action of potassium and its ethoxide towards quinone has been studied by Astre (Bull. Soc. chim. 1895, iii. 13, 1037, 1070). By leading oxygen through warm solutions of quinone in alcoholic potash the salts KHC_6O_6 and $K_2C_6O_6$ are produced. On adding concentrated alcoholic potash to a dilute ethereal solution of quinone, a decomposable, blue, crystalline salt, $KC_6H_3O_2{\cdot}H_2O$, is precipitated.

Hydrogen sulphide reduces quinone to

quinol. Wöhler also obtained compounds, $C_{12}H_{10}O_4S_2$ (?) and $C_{12}H_{12}O_4S$ (Annalen, 1849, 69, 294). Quinone is reduced by yellow ammonium sulphide in the cold; if heated, a bluish-violet dyestuff is produced (Willgerodt, Ber. 1887, 20, 2470). Of more interest is the production of a black substantive dye, capable of technical application (Vidal, D. R. P. 84632, 1893).

A mixture of 10 kilos. of quinone, 5 kilos. of sulphur, 4 kilos. of ammonium chloride and 6 kilos. of caustic soda are heated in a closed vessel for 6 hours at 160°–210°. After cooling, the mass is crushed and can be used directly for dyeing. The solution in alkaline carbonates or sulphides has a bottle-green colour, unmordanted vegetable fibres are dyed a greenish-black; a black-blue is obtained by subsequent treatment with ferric chloride or potassium dichromate. The bottle-green alkaline solutions give a brownish-red precipitate with hydrochloric acid which blackens on exposure to the air. When the alkaline solution is oxidised in the air, a dirty green precipitate, insoluble in alkaline carbonates, is produced.

Quinone gives an indigo-coloured addition product, $2C_6H_4O_2{\cdot}H_2S_3$, with hydrogen persulphide. M. M. Richter regards this as an oxonium salt (Ber. 1910, 43, 3599).

With compounds of the type HSR, quinol derivatives, $C_6H_3(SR)(OH)_2$, are formed. These can be oxidised to quinones, $C_6H_3(SR)O_2$, whieh will react in turn with the sulphur compound. By alternating the reactions, all the hydrogen atoms of quinone may be replaced by SR groups. The mono-, di-, and tri-chloroquinones also react quite smoothly without the chlorine atoms being displaced. For example, the salt

$$C_6H_3(OH)_2(S{\cdot}SO_3K)$$

may be obtained by mixing 43·2 parts of quinone in 150 parts of glacial acetic acid with 150 parts of sodium thiosulphate in 200 parts of water and salting out with potassium chloride. If the salt is reduced by zinc-dust and acid in presence of ether, thiolquinol, $C_6H_3(SH)(OH)_2$, m.p. 119°–120°, is obtained. Other compounds containing the group ·SH (or ·SM) which have been employed are thiobenzoic acid, potassium xanthogenate, potassium thiocyanate and sodium trithiocarbonate (Badische Anilin- und Soda-Fabrik, D. R. P. 175070, 1905).

The compounds obtained according to the foregoing method may be used for the manufacture of sulphur dyes. The necessary materials are (1) benzoquinone or one of its halogen derivatives, (2) a compound containing the group SR, (3) a *mono-* or *as-di*-alkylated *p*-diaminethiosulphonic acid or the corresponding mercaptan or disulphide. The following example is given in the patent (B. A. S. F., D. R. P. 167012, 1905).

25 parts of benzoquinone are dissolved in 100 parts of glacial acetic acid; the solution is cooled to 5°–10°, and a solution of 13·5 parts of sodium hydrosulphide in 60 parts of water run in. To the clear brown solution, a solution of 25 parts of dimethyl-*p*-phenylenediaminethiosulphonic acid in 200 parts of water and 15 parts of 20 p.c. ammonia is added, and then 250 parts of caustic soda lye of 40°Bé. The clear green solution is heated for 2 hours at 60° when the greater part of the colouring matter is precipitated as a dark blue powder. The filtrate from the dyestuff yields a further amount by blowing air through it. (*See* further, B. A. S. F., D. R. PP. 178940, 1905; 179225, 1905.)

For the volumetric estimation of quinone, sulphurous acid (Nietzki, Annalen, 1882, 215, 128) or hydriodic acid and thiosulphate (A. Valeur, Compt. rend. 1899, 129, 552; Willstätter and Dorogi, Ber. 1909, 42, 2165; Wieland, *ibid.* 1910, 43, 716; Willstätter and Majima, *ibid.* 1910, 43, 1171) may be used.

Quinone-imine $C_6H_4O(:NH)$. By oxidising *p*-aminophenol in ethereal solution with silver oxide. Colourless crystals (Willstatter, Ber. 1904, 37, 1494, 4605).

Quinone-imine condenses directly with aromatic bases giving leuco-indophenols (Akt. Ges. Anilin-F., D. R. P. 184601, 1905)

$$O:C_6H_4:NH+C_{10}H_7{\cdot}NH_2 = HO{\cdot}C_6H_4{\cdot}NH{\cdot}C_{10}H_7{\cdot}NH_2$$

A cold aqueous solution of quinone-imine, obtained from 14·6 kilos. of *p*-aminophenol and the calculated amount of ferric chloride, is mixed with a concentrated solution of 18 kilos. of α-naphthylamine hydrochloride. The leuco-indophenol separates immediately and is filtered off and washed. It may be used directly in the preparation of sulphur dyestuffs.

Quinone-chloroimine $C_6H_4O(:NCl)$, is obtained from *p*-aminophenol or *p*-phenetidine and bleaching powder solution (Schmitt and pupils, J. pr. Chem. 1873, ii. 8, 2; 1878, ii. 19, 315; 1881, ii. 23, 435; Hirsch, Ber. 1880, 13, 1903). Willstätter and Mayer use a solution of sodium hypochlorite and *p*-aminophenol hydrochloride (Ber. 1904, 37, 1499). Bamberger and Tschirner obtained it mixed with other products by the action of hypochlorous acid on aniline (*ibid.* 1898, 31, 1523).

Quinone-chloroimine forms yellow crystals, m.p. 85°, explodes on further heating. Volatile with steam, easily soluble in organic solvents and hot water, difficultly in cold. Hydrolysed to ammonium chloride and quinone, reduced to *p*-aminophenol, soluble in cold concentrated sulphuric acid and fuming nitric acid without decomposition. Yields mono-, di-, and trichloroaminophenols with concentrated hydrochloric acid. Used for synthetic purposes and in the preparation of dyestuffs (Clayton Aniline Co., D. R. P. 106036, 1898; Akt. Ges. Anilin-F., D. R. P. 124872, 1899).

An example of the preparation of a black sulphur dyestuff is taken from a subsequent patent.

10 parts of quinone-chloroimine are suspended in a concentrated solution of 15·5 parts of sodium thiosulphate; 240 parts of 33 p.c. sulphuric acid are added in the cold and the mixture slowly warmed. The colour of the solution becomes reddish-brown, then black-brown: finally the mixture is boiled for 1 or 2 hours. After cooling, the precipitate is collected, washed, dissolved in dilute caustic soda or sodium carbonate and salted out. The alkaline solutions have a brownish-black shade. A similar dyestuff may be obtained from chloroquinonechloroimine (Akt. Ges. Anilin-F., D. R. P. 127834, 1899).

Quinone chloroimine condenses with aromatic amines and phenols, giving indophenols. The reaction can be carried out when the chloroimine is dry or in paste. Examples are given using α-naphthol, α-naphthylamine, *o*-toluidine and diphenylamine (Weiler-ter-Meer, D. R. P. 189212, 1906, lapsed in 1909).

Quinone-methylimine $C_6H_4O(:NCH_3)$. By oxidising *p*-methylaminophenol dissolved in ether with silver oxide or lead peroxide. Explosive needles (Willstätter and Pfannenstiehl, Ber. 1905, 38, 2244).

Quinone-phenylimine $C_6H_4O(:N\cdot C_6H_{15})$. By oxidising *p*-hydroxydiphenylamine dissolved in benzene with yellow mercuric oxide, m.p. 97° (Bandrowski, Monatsh. 1888, 9, 134).

Quinoneanil oxide $O:C_6H_4:N(C_6H_5):O$, m.p. 142° (Wieland and Roth, Ber. 1920, 53, 210).

Quinone-p-*tolylimine* $C_6H_4O(:N\cdot C_6H_4\cdot CH_3)$, m.p. 70° (Bandrowski).

Quinone-p-*anisylimine*

$$C_6H_4O(:N\cdot C_6H_4\cdot OCH_3)$$

m.p. 84° (Willstätter and Kubli, Ber. 1909, 42, 4135).

The violet colouring matter obtained by oxidising *p*-aminophenol with ferric chloride appears to possess the constitution

$$C_6H_3(OH)(NH_2)\cdot N:C_6H_4:O,HCl$$

(Willstätter and Piccard, Ber. 1909, 42, 1902). The indophenols (*q.v.*) may be regarded as derivatives of the quinone arylimines or aryldiimines; their structure is represented by $O:C_6H_4:N\cdot C_6H_4\cdot NH_2$ or $HO\cdot C_6H_4\cdot N:C_6H_4:NH$.

Quinone-diimine $C_6H_4(:NH)_2$. By oxidising *p*-phenylenediamine in ethereal solution with silver oxide (Willstätter and Pfannenstiehl, Ber. 1904, 37, 4606), or by passing ammonia into an ethereal suspension of the dihydrochloride. Colourless crystals, discoloured at 75°, m.p. 124°. Explodes with concentrated sulphuric acid unless mixed carefully. *Dihydrochloride*, colourless when pure, is produced by passing hydrogen chloride into a solution of the diimine in ether or benzene, or from quinone-dichlorodiimine and hydrochloric acid (Willstätter and Meyer, *ibid.* 1904, 37, 1494). *See* also Pringsheim, *ibid.* 1905, 38, 3354; Kehrmann, *ibid.* 3777). *Monohydrobromide*, from bromine on ethereal *p*-phenylene diamine (Jackson and Calhane, 1902, 35, 2496) is probably a 'meriquinonold' compound. *Di*-p-*nitrophenolate* $C_6H_4(:NH_2\cdot O\cdot C_6H_4\cdot NO_2)_2$, m.p. 59°; pale coloured (A. Knorr, Ber. 1911, 44, 1503).

The quinone-diimines may be used directly for the preparation of leuco-indophenols (Akt. Ges. Anilin-F., D. R. P. 184651, 1905). The solution obtained by oxidising 13·6 kilos. of dimethyl-*p*-phenylenediamine with ferric chloride is added to a solution of 9·4 kilos. of phenol in water, stirring and cooling meanwhile. The leucoindophenol separates rapidly; the precipitation is completed by salting out.

The solution of quinone-diimine-sulphonic acid obtained by oxidising 18·8 kilos. of *p*-phenylenediamine-sulphonic acid with ferric chloride is allowed to flow into a cooled solution of 10·8 kilos. of *o*-cresol. A precipitate is produced: it is soluble in alkalis.

Quinone-dichlorodiimine $C_6H_4(:NCl)_2$. By adding to a solution of *p*-phenylenediamine hydrochloride, a solution of bleaching powder (Krause, Ber. 1879, 12, 47) or sodium hypochlorite (Willstätter and E. Meyer, *ibid.* 1904, 37, 1498). Volatile with steam, soluble in organic solvents, m.p. 126° (with decomposition). Reduced by stannous chloride, sulphurous acid and sodium amalgam to *p*-phenylene diamine. With hydrochloric acid gives quinone-diimine dihydrochloride or tetrachloro-*p*-phenylenediamine. Used synthetically, *e.g.* the compound $C_{10}H_6\langle{}^{O}_{N}\rangle C_6H_3:NH$ is produced on condensation with β-naphthol (Nietzki and Otto, Ber. 1888, 21, 1745). Has been employed in the production of indophenols, azines (Bayer and Co., D. R. P. 84504, 1894) and sulphur dyestuffs.

Whilst most of the *indophenols* have not been used to a large extent for dyeing, they have proved to be useful materials in the preparation of sulphur dyestuffs. This holds good for their leuco-compounds, the 4:4′-aminohydroxy-derivatives of secondary aromatic amines. The indophenols were first prepared by the action of nitrosodialkylanilines on phenols (Koechlin and Witt, D. R. P. 15915, 1881; Majert, D. R. P. 18628, 1881; Cassella, D. R. PP. 18903, 1881; 19291, 1881; 20850, 1882; Bayer and Co., D. R. P. 41512, 1887). A number of patents relate to the preparation of indophenols by oxidation of a mixture of a *p*-diamine and a phenol (Akt. Ges. Anilin-F., D. R. PP. 160710, 1904; 168229, 1904; 179294, 179295, 1905); *p*-phenylenediamine-sulphonic acid may also be employed (Griesheim-Elektron, D. R. P. 171028, 1904).

For the preparation of the simplest indophenol, $NH_2\cdot C_6H_4\cdot N:C_6H_4:O$ or

$$NH:C_6H_4:N\cdot C_6H_4\cdot OH$$

10·8 parts of *p*-phenylenediamine and 10 parts of phenol are dissolved in 1500 to 2000 parts of water. The solution is well stirred at 10°–15° and a paste of 48 parts of lead peroxide in a solution of 50 parts of disodium phosphate and 35 parts of sodium bicarbonate added. The indophenol is at once produced and separates in brassy leaflets (D. R. P. 179294). The phosphate and carbonate are not essential (D. R. P. 179295). 21·6 parts of *p*-phenylenediamine and 20 parts of phenol are dissolved in 3000 parts of water, stirred at 10°–15°, and a paste of 96 parts of lead peroxide added. The indophenol is extracted from the mixture with hydrated lead oxide by means of alcohol or hot water. M.p. 160°. For reactions and conversion into 7-anilinosafranol, *see* Heller, Annalen, 1912, 392, 16.

The indophenols can also be obtained from the chloroimines and monoximes of *p*-quinones by condensation with amines in presence of 70 p.c. sulphuric acid. Amino-derivatives of the indophenols are formed when *m*-diamines are used (*see* Ger. Pat. applications of Ges. Chem. Ind. Basel, A. 10389; Farbwerke Höchst, 11485).

Indophenols are obtained directly from quinone dichlorodiimine and compounds such as α-naphthol. A solvent is unnecessary: thus the reaction may be carried out by grinding a mixture of 164 parts of α-naphthol, 100 parts of

the dichlorodiimine and 500 parts of common salt until the dichlorodiimine has disappeared (Weiler-ter-Meer, D. R. P. 189212, 1906, lapsed 1909).

Quinone-dichlorodiimine yields a black sulphur dye if the amount obtained from 50 parts of *p*-phenylenediamine is suspended in a concentrated solution of 100 parts of sodium thiosulphate, 1000 parts of 33 p.c. sulphuric acid added and the mixture slowly warmed (Akt. Ges. Anilin-F., D. R. P. 127834, 1899).

Quinone-dibromodiimine $C_6H_4(:NBr)_2$. Explodes at 86° (Krause, Ber. 1879, 12, 50).

Quinone-monomethyldiimine

$$C_6H_4(:NH)(:N\cdot CH_3)$$

Colourless (Willstätter and Piccard, Ber. 1908, 41, 1458).

Quinone-s-*dimethyldiimine* $C_6H_4(:NCH_3)_2$. From *s*-dimethyl-*p*-phenylenediamine in ether with silver oxide. Colourless crystals, m.p. 92·5°–93°. Explodes with concentrated hydrochloric or sulphuric acid (Willstätter and Pfannenstiehl, *ibid.* 1905, 38, 2244). From *as*-dimethyl-*p*-phenylenediamine, Wurster's 'meriquinonoid' salt can be obtained, also a colourless imonium nitrate,

$$C_6H_4[:NH\cdot HNO_3][:N(CH_3)_2\cdot NO_3]$$

Quinone-monophenyldiimine

$$C_6H_4(:NH)(:N\cdot C_6H_5)$$

is obtained from *p*-aminodiphenylamine by oxidation with lead peroxide (Heucke, Annalen, 1889, 255, 193) or silver oxide (Willstätter and Moore, Ber. 1907, 40, 2665). Also by oxidation of aniline with potassium permanganate (Bamberger and Tschirner, *ibid.* 1898, 31, 1526). Brown crystals with $3CH_3OH$; m.p. 208°. The acetic acid solution has a bluish-green colour. *Polymeric form* $C_{36}H_{30}N_6$, m.p. 217°–218° (Willstätter and Kubli, Ber. 1909, 42, 4135). Quinone-phenyldiimine is of interest on account of its relation to aniline-black (*q.v.*).

Quinone-p-*tolylimine*, m.p. 114°, combines with 1 or 2 HCl *Termolecular form*, m.p. 187° (W. and K., *l.c.*).

Quinone-p-*anisylimine*, m.p. 71°–72°; *mono-* and *di-hydrochlorides*. *Termolecular form* darkens at 150°, softens at 170°, melts at 176° (W. and K.).

Quinone-mono-p-*aminophenyldiimine*

$$NH:C_6H_4:N\cdot C_6H_4\cdot NH_2$$

is the simplest indamine. Its greenish-blue, water-soluble, unstable salts are produced by oxidising a mixture of aniline and *p*-phenylenediamine salts. An excess of mineral acid hydrolyses indamine with production of quinone. On heating with an aqueous solution of an aniline salt, phenosafranine is formed.

Bindschedler's green

$$(CH_3)_2Cl\cdot N:C_6H_4:N\cdot C_6H_4\cdot N(CH_3)_2$$

is the tetramethyl- derivative of the simplest indamine. It is produced by oxidising a mixture of dimethylaniline and dimethyl-*p*-phenylenediamine. It is of no technical importance, being easily decomposed by acid and alkalies.

Quinone diphenyldiimine $C_6H_4(:N\cdot C_6H_5)_2$. By oxidising diphenylamine (preferably with aniline) by potassium permanganate; shining brownish-yellow crystals, m.p. 176°–180° (Bandrowski, Monatsh. 1886, 7, 375; 1887, 8, 478). Easily reduced to diphenyl-*p*-phenylenediamine; oxidised to quinone by manganese dioxide and dilute sulphuric acid.

Quinone-monoxime $C_6H_4O(:NOH)$. By boiling nitroso-dimethylaniline with soda (Baeyer and Caro, Ber. 1874, 7, 809), by the action of nitrous acid (*ibid.* 963) or nitrosyl sulphate (Groves and Stenhouse, Chem. Soc. Trans. 1877, 32, i. 544) on phenol, by dilute solution of hydroxylamine hydrochloride on quinone (Goldschmidt, Ber. 1884, 17, 805) and by the hydrolysis of nitrosoanisole, $NO\cdot C_6H_4\cdot OCH_3$ (Baeyer and Knorr, *ibid.* 1902, 35, 3035). It is easily prepared by dissolving equivalents of phenol and sodium nitrite in water, adding a large amount of crushed ice and pouring in dilute sulphuric acid with continual stirring. The compound separates in the course of some hours, crystalline and practically pure. Modified methods of preparation are given by Hugo Koehler (D. R. P. 25469, 1883) and Nietzki and Guitermann (Ber. 1888, 21, 429).

The constitution has been already discussed; for the analogous cases of the naphthaquinone-oximes (nitrosonaphthols), *see* C. H. Sluiter (Ber. 1911, 44, 1327).

On heating, quinone-oxime decomposes at 120°–130°. Dissociation constant,

$$k=3300\times10^{-10}$$

(Hantzsch and Barth, Ber. 1902, 35, 219; *cf. ibid.* 1003). Behaviour towards ammonia (Hantzsch and Dollfuss, *ibid.* 1902, 35, 262).

Quinone-oxime gives metallic salts

$$C_6H_4O(:NOM)$$

the acyl derivatives are of type

$$C_6H_4O(:NO\cdot CO\cdot R)$$

and the alkyl compounds have a similar constitution, $C_6H_4O(:NOR)$. The isomeric nitrosophenylethers, $NO\cdot C_6H_4\cdot OR$, are obtained by the action of Caro's acid on the *p*-alkyloxyanilines (Baeyer and Knorr, Ber. 1902, 35, 3034).

Benzoyl derivative, m.p. 172°–174° (Walker, Ber. 1884, 17, 400; Bridge, Annalen, 1893, 277, 97); *ethyl carbonate*, m.p. 109° (Walker); *phenylcarbamate*, decomposes at 110° without fusion (Goldschmidt, Ber. 1889, 22, 3105).

Quinone-oxime-o-*nitrophenylhydrazone*

$$C_6H_4(:NOH)(:N\cdot NH\cdot C_6H_4\cdot NO_2)$$

From quinone-oxime and *o*-nitrophenylhydrazine; the latter will also react with quinone itself yielding *o*-nitrobenzeneazophenol. *p*-Nitrophenylhydrazine gives a hydrazone with quinone-oxime but not with quinone itself. *m*-Nitrophenylhydrazine gives neither hydroxyazo-compounds nor quinone-oxime hydrazones (Borsche, Annalen, 1904, 334, 143; 1905, 340, 85; 1906, 343, 176; 1907, 357, 171).

Quinone-oxime gives dyestuffs on heating with mineral acids. 10 parts of nitrosophenol are warmed with 100 parts of 50 p.c. sulphuric acid for 2–3 hours at 100°, the black precipitate is filtered off, washed and dried. The product is insoluble in water, cotton is coloured brown by the alkaline solution; fast shades are obtained if the dyebath contains sodium sulphide and the goods are subsequently treated with blue vitriol or bichromate solution (Clayton Aniline Co., D. R. P. 106036, 1898).

Nitrosophenol reacts with thiosulphates, this reaction forms the starting point for the

sulphur dyestuff, Clayton Black D. (D. R. P. 106030, 1898).

The oximes of quinones, when subjected to the action of phosphorus pentachloride (or other acid chlorides), undergo a Beckmann transformation which probably leads to the formation of an enlarged ring (E. Beckmann and O. Liesche, Ber. 1923, 56, 1). Earlier experiments by W. Borsche and W. Jacobs (Ber. 1914, 47, 354), and W. Borsche aud W. Sander (*ibid.* 2815), pointed to fusion of the ring, in the case of isatoxime, but Bechmann and Liesche (with A. Philippovich von Philippsberg) find that *p*-benzoquinonemonoxime may be made to yield a compound, $CO\langle^{CH:CH\cdot CO}_{CH:CH\cdot NH}$, yellowish-brown needles, m.p. 224°.

Quinone-dioxime $C_6H_4(:NOH)_2$ is obtained by the action of hydroxylamine hydrochloride on quinone or its monoxime or on quinol (Nietzki and Kehrmann, Ber. 1887, 20, 614); on *p*-nitrosoaniline (O. Fischer and Hepp, *ibid.* 1888, 21, 685); and on benzyl-*p*-nitrosoaniline (Böddinghaus, Annalen, 1893, 263, 304). Freshly made quinone-monoxime is covered with 50 parts of water and one molecular proportion each of hydroxylamine hydrochloride and hydrochloric acid added. After standing 6–8 days, the oxime is filtered off, washed with dilute ammonia, dissolved in strong ammonia and precipitated by carbon dioxide. Needles, decomposes about 240°. Very weak acid (Farmer and Hantzsch, Ber. 1899, 32, 3107). Oxidised by alkaline ferricyanide to *p*-dinitrosobenzene. A polymerised anhydride has been described (Farmer and Hantzsch).

Two *diacetyl derivatives* are known; the *syn*-form, m.p. 147°; the *anti*-form, m.p. 190° (with decomposition) (Kehrmann, Ber. 1895, 28, 341).

Salts of a *p-dinitroxime*, *e.g.* $C_6H_4(:NO\cdot OK)_2$, have been obtained by reduction of *p*-dinitrobenzene (Meisenheimer, Ber. 1903, 36, 4174; 1906, 39, 2526).

Quinone in virtue of its ketonic character also yields *mono-* and *di- semicarbazones*, an *oxime-semicarbazone* and products with one or two molecules of aminoguanidine (Thiele and Barlow, Annalen, 1898, 302, 329).

2-**Chloro**-*p*-**Benzoquinone** $C_6H_3ClO_2$. By distilling copper quinate with salt, manganese dioxide and dilute sulphuric acid (Staedeler, Annalen, 1849, 69, 302). By oxidising chloroquinol with chromic acid (Levy and Schultz, *ibid.* 1881, 210, 145). From *o*-chloro-*p*-aminophenol (Kollrepp, *ibid.* 1886, 234, 14).

Pale yellow (not yellowish-red) crystals (J. Schmidlin, Ber. 1911, 44, 1700), m.p. 157°. Molecular heat of combustion at constant pressure, 618·2 cal. (A. Valeur, Ann. Chim. 1900, vii. 21, 487). Gives a dichloride and with hydrogen chloride yields 2 : 5- and 2 : 3-dichloroquinols (Peratoner and Genco, Gazz. chim. ital. 1894, 24, ii. 386, 394). Reacts with bases (Niemeyer, Annalen, 1888, 228, 322, 324).

2-*Chloroquinone*-4-*Chloroimine*, m.p. 87° (Kollrepp). Has been used for making sulphur dyestuffs (Akt. Ges. Anilin-F., D. R. P. 127834, 1899).

2-*Chloroquinone-dichlorodiimine*, m.p. 83°–84° (Cohn, Chem. Zentr. 1902, I. 386).

2-*Chloroquinone*-4-*oxime* $C_6H_3ClO(:NOH)$, m.p. 141° (Kehrmann, Ber. 1888, 21, 3316; *ibid.* 1898, 303, 5; Bridge, *ibid.* 1893, 277, 100). The *methyl ether*, *α*- (m.p. 123°) and *β*- (m.p. 114°–115°), *modifications* (Bridge, *ibid.* 1893, 277, 90; Kehrmann, *ibid.* 1894, 279, 35), *α-Benzoyl derivative*, m.p. 197° (B.) or 192° (Kehrmann, Ber. 1894, 27, 218); *β-derivative*, m.p. 162° (K.). Two stereoisomeric *acetyl derivatives*, m.p. 166°–167° and 136°–137° (Kehrmann and Grah, Annalen, 1898, 303, 6).

2-*Chloroquinone-dioxime*, greyish needles (Kehrmann, Ber. 1888, 21, 3317; Kehrmann and Grah, *l.c.*). *Diacetyl derivative*, m.p. 171°–172°.

2 : 3-**Dichloro**-*p*-**Benzoquinone** $C_6H_2Cl_2O_2$, m.p. 96° (Peratoner and Genco, Gazz. chim. ital. 1894, 24, ii. 379; Oliveri, *ibid.* 1897, 27, ii. 584). These results are doubted by A. J. den Hollander (Rec. trav. chim. 1920, 39, 481). *See* also Eckert and Endler, J. pr. chem. 1922, ii. 104, 81.

2 : 5-**Dichloro**-*p*-**Benzoquinone**, m.p. 161° (Staedeler, Annalen, 1849, 69, 309; Carius, *ibid.* 1867, 143, 316; Levy and Schultz, *ibid.* 1881, 210, 150; Möhlau, Ber. 1886, 19, 2010; Hantzsch and Schniter, *ibid.* 1887, 20, 2279; Ling, Chem. Soc. Trans. 1892, 61, 558; Bandrowski and Prokopeczko, Bull. Acad. Sci. Cracow, 1901, 441).

Compound with *m*-nitro-aniline (Niemeyer, Annalen, 1888, 228, 325); *dichlorodiimine*, m.p. 134°–135° (Möhlau); *diphenyldiimine*, m.p. 220° (Bandrowski and Prokopeczko); *monoxime* and its *acetyl derivative* (Kehrmann and Grah, Annalen, 1898, 303, 13); *dioxime* (Kehrmann).

2 : 6-**Dichloro**-*p*-**Benzoquinone**, m.p. 120°. From 2 : 4 : 6-trichlorophenol and fuming nitric acid (Faust, Annalen, 1869, 149, 153) or by acting on an alcoholic solution of trichlorophenol with nitrous fumes (Weselsky, Ber. 1879, 3, 646). *See* also Armstrong (Zeitsch. Chem. 1871, 521); Levy (Ber. 1883, 16, 1446); Kehrmann and Tiesler (J. pr. Chem. 1889, ii. 40, 481); Ling (Chem. Soc. Trans. 1892, 61, 559); Kollrepp (Annalen, 1886, 234, 14).

Heat of combustion at constant pressure, 580·4 cal. (Valeur, Ann. Chim. 1900, vii. 21, 491).

Treated with alcoholic ammonia, the chlorine atoms are replaced by amino-groups (Kehrmann and Tiesler). Compound with *m*-nitroaniline (Niemeyer); *chloroimine*, m.p. 67°–68° (Kollrepp); *monoxime*, decomposes at 140° (Kehrmann, Ber. 1888, 21, 3318).

Trichloro-*p*-**benzoquinone** $C_6HCl_3O_2$. 2 parts of phenol-*p*-sulphonic acid obtained by heating equal weights of phenol and sulphuric acid at 100° are dissolved in a hot solution of 4 parts of potassium chlorate and excess of hydrochloric acid added. After standing 24 hours, finish the reaction by blowing in steam, filter and wash with hot water, then cold alcohol. Suspend the mixture of tri- and tetra-chloroquinones so obtained in 10 parts of water and lead in sulphur dioxide for 10 minutes. When hot, the trichloroquinol remains dissolved, filter and oxidise with fuming nitric or chromic acid (Knapp and Schultz, Annalen, 1881, 210, 174; Graebe, *ibid.* 1868, 146, 9; 1891, 263, 28; Stenhouse, *ibid.* Spl., 1868, 6, 218). For other methods of preparation, reactions and derivatives, *see* Staedeler (*ibid.* 1849, 69, 618); Carstanjen (Ber. 1869, 2, 633); Schmitt and Andresen (J. pr.

Chem. 1881, ii. 23, 436; 1881, ii. 24, 434; 1883, ii. 28, 422); MacPherson and Fischer (J. Amer. Chem. Soc. 1900, 22, 141); Niemeyer (Annalen, 1888, 228, 325); E. Léger (Compt. rend. 1908, 146, 694); Jacobson, Bartsch and Steinbreck (Annalen, 1909, 367, 304).

Large yellow leaflets, m.p. 165°–166°; molecular heat of combustion at constant pressure 548·8 cal. (Valeur, Ann. Chim. 1900, vii. 21, 496).

Tetrachloro-*p*-benzoquinone or **Chloranil** $C_6Cl_4O_2$, is frequently produced from aromatic compounds, *e.g.* by the action of chlorine on an alcoholic solution of chloroisatin (Erdmann, Annalen, 1843, 48, 309) or by the action of potassium chlorate and hydrochloric acid on aniline (Fritzsche, Bull. Sci. St. Petersb., 1843, i. 103), phenol (Hofmann, Annalen, 1844, 52, 57), quinic acid (Staedeler, *ibid.* 1849, 69, 326), salicylic and nitrosalicylic acids (Hofmann); dinitrosalicylic acid (Stenhouse, *ibid.* 1851, 78, 4), tyrosin (Staedeler, *ibid.* 1860, 116, 99); *m*-aminobenzoic acid (Erlenmeyer, Jahresb. 1861, 404). It is also obtained by the action of fuming nitric acid on pentachlorophenol (Merz and Weith, Ber. 1872, 5, 460) and on 1 : 2 : 4 : 5-tetrachlorobenzene, but not on its isomers (Beilstein and Kurbatow, Annalen, 1878, 192, 236). For other methods of preparation and purification, some involving separation from trichloroquinone, *see* Graebe (*ibid.* 1891, 263, 23), Andresen (J. pr. Chem. 1883, ii. 28, 425), Knapp and Schultz (Annalen, 1881, 210, 176), Stenhouse (*ibid.* Spl., 1868, 6, 209), Barral (Bull. Soc. chim. 1894, iii. 11, 708), Elbs and Brunnschweiler (J. pr. Chem. 1895, ii. 52, 560), Witt and Toeche-Mittler (Ber. 1903, 36, 4390), Bouveault (Ann. Chim. 1908, viii. 13, 142), Brazier and McCombie (Chem. Soc. Trans. 1912, 101, 968).

Originally, phenol was usually employed for the preparation of chloranil. Graebe found a purer product was obtained from *p*-phenylenediamine, the yield being also better, whilst Witt and Toeche-Mittler (*l.c.*) obtained the best results with 2 : 6-dichloro-*p*-phenylenediamine.

A lukewarm solution of 16·4 grms. of potassium chlorate is added gradually to a solution of 28 grms. of *p*-nitroaniline in 250 c.c. of concentrated hydrochloric acid at 50°. Much water is added and the precipitate collected. Yield of crude product, 36 grms. (87 p.c. of theory). Once recrystallised from glacial acetic acid or acetic acid and alcohol gives a dichloronitroaniline, melting at 185°–187°.

12 grms. of dichloronitroaniline in 300 c.c. of concentrated hydrochloric acid are reduced with 13 grms. of granulated tin; to the boiling hot solution 10 grms. of potassium chlorate crystals are added: 11 grms. of chloranil, m.p. 268°–270°, are obtained. One crystallisation from toluene raises the melting-point to 285°–286°. On a large scale, yields up to 90 p.c. of the theoretical were obtained.

Chloranil sublimes readily, m.p. (in sealed tube) 290°. Molecular heat of combustion at constant pressure, 519 cal. (Valeur, Ann. Chim. 1900, vii. 21, 499). Other properties and reactions, *see* Graebe (Annalen, 1868, 146, 12; 1891, 263, 19), Sarauw (*ibid.* 1881, 209, 125), Levy and Schultz (Ber. 1880, 13, 1430; Annalen, 1881, 210, 154), Knapp and Schultz (*ibid.* 1881, 210, 189), Niemeyer (*ibid.* 1888, 228, 326), Jackson and Torrey (Amer. Chem. J. 1898, 20, 427), Imbert and Pagès (Bull. Soc. chim. 1898, iii. 19, 575), Imbert (Compt. rend. 1901, 133, 162), Richter (Ber. 1911, 44, 3469).

Technically, chloranil has been used for oxidising leucobases to dyestuffs (Meister, Lucius and Brüning, D. R. P. 11412, 1879). Heated with aromatic amines, dyestuffs are produced (Greiff, Ber. 1879, 12, 1610). At one time spirit soluble dyes, known as 'chloranil blue,' were prepared from chloranil and derivatives of diphenylamine. In 1879, Meister, Lucius and Brüning patented the production of violet, blue, or green dyes by heating dimethylaniline, methyldiphenylamine (or its homologues) and benzyldiphenylamine (or its homologues) respectively with chloranil. The chloranil behaved simply as an oxidising agent (D. R. P. 11811, lapsed 1882; compare also Ber. 1879, 12, 1952; 1883, 16, 2005, 2904, 3044; 1884, 17, 100).

Quinone-imide dyestuffs are obtained by condensing chloranil with amino-hydroxy-aromatic acids (von Heyden, D. R. P. 198163, 1898).

2-**Bromo-*p*-benzoquinone** $C_6H_3BrO_2$, m.p. 55°–56° (Sarauw, Annalen, 1881, 209, 106). *Oxime* (?), a mixture (Kehrmann, Ber. 1888, 21, 317). 2 : 4-*Dibromophenylimine*, m.p. 112° (Smith and Orton, Chem. Soc. Trans. 1908, 93, 318).

2 : 5-**Dibromo-*p*-benzoquinone** $C_3H_2Br_2O_2$, m.p. 188° (Benedikt, Monatsh. 1880, 1, 346; Sarauw, Annalen, 1881, 209, 113).

2 : 6-**Dibromo-*p*-benzoquinone**, m.p. 131° (Levy and Schultz, Annalen, 1881, 210, 158; Henrichsen, *ibid.* 1889, 253, 286; Thiele and Eichwede, Ber. 1900, 33, 673; van Erp, Rec. trav. chim. 1911, 30, 270). *Hydroxyphenylimine* $C_6H_2Br_2O(:N\cdot C_6H_4OH)$ (Möhlau, *ibid.* 1883, 16, 2845). *Diimine hydrobromide* (Jackson and Calhane, *ibid.* 1902, 35, 2495).

2 : 6-*Dibromo*-1 : 4-*dimethylthioniumquinone* $C_6H_2Br_2[:S(CH_3)]_2:O$, m.p. 251°–252°; by the action of alkali on $C_3H_2Br_2[S(CH_3)_2I]OH$ (Zincke and Glahn, Ber. 1907, 40, 3046).

2 : 6-*Dibromo-p-benzoquinone*-4-*oxime* blackens at 160°, explodes at 168°–175° (O. Fischer and Hepp, Ber. 1888, 21, 674; Kehrmann, *ibid.* 3318; Forster and Robertson, Chem. Soc. Trans. 1901, 79, 687; van Erp, *loc. cit.*): *acetyl derivative*, m.p. 122°; *benzoyl derivative*, m.p. 197°; 4-Chloroimine, m.p. 78° (Möhlau, Ber. 1883, 16, 2845; Friedländer and Stange, *ibid.* 1893, 26, 2262).

Two other dibromobenzoquinones melting at 76° (Böhmer, J. pr. Chem. 1881, ii. 24, 464) and 88° (Prunier, Ann. Chim. 1878, v. 15, 67) have been described.

Tribromo-*p*-benzoquinone, m.p. 147° (Sarauw, Annalen, 1881, 209, 120; Prunier, *l.c.*; Stenhouse, Annalen, Spl., 1872, 8, 20; Heermann, Ber. 1877, 10, 110).

Tetrabromo-*p*-benzoquinone or **bromanil** $C_6Br_4O_2$, m.p. 300°. For preparation, *see* Stenhouse (Annalen, 1854, 91, 307; Spl., 1872, 8, 18); Sarauw (Annalen, 1881, 209, 126); Hübner (*ibid.* 1867, 143, 255); Hlasiwetz and Habermann (*ibid.* 1871, 159, 320); Schunck and Marchlewski (*ibid.* 1894, 278, 348); Graebe and Weltner (*ibid.* 1891, 263, 33); Losanitsch (Ber. 1882, 15, 374); Ling (Chem. Soc. Trans. 1892, 61, 568); Simonis and Wenzel (Ber. 1900, 33, 421); Auwers and Büttner (Annalen, 1898,

302, 133, 142). The method of Graebe and Weltner is to be recommended. Numerous chloro-bromo-quinones have been prepared.

2 : 5-**Diiodo-*p*-benzoquinone,** m.p. 157°–159° (Metzeler, Ber. 1888, 21, 2555). Tetraiodo-*p*-benzoquinone or iodanil, $C_6I_4O_2$, m.p. 282°–284°, is obtained by boiling bromanil with potassium iodide in acetone solution. The dibromodiiodo- and bromotriiodo-quinones (m.ps. 258°–259° and 253°–254°) are also formed (Torrey and Hunter, J. Amer. Chem. Soc. 1912, 34, 702). By alkaline hydrolysis and subsequent acidification, iodanilic hemi-ether $(OH{\cdot}C_6I_2O_2)_2O$, is formed (Loring Jackson and Bolton, J. Amer. Chem. Soc. 1914, 36, 551, 1473). With nitric acid, iodic anhydride and di-iodomaleic acid are obtained (Clarke and Bolton, *ibid.* p. 1899). Partial reduction gives octaiodo-quinhydrone (Loring Jackson and Bolton, Ber. 1912, 45, 871).

2 : 6-**Diiodo-*p*-benzoquinone,** m.p. 178° (R. Seifert, J. pr. Chem. 1883, ii. 28, 438; Kehrmann and Messinger, Ber. 1893, 26, 2377; Kehrmann, J. pr. Chem. 1887, ii. 37, 336; Willgerodt and Arnold, Ber. 1901, 34, 3351). *Dibromodiiodo-*, *Bromotriiodo,* and *Tetraiodo-p-benzoquinones* melt at 258°–259°, 253°–254°, and 282°–284° respectively (Torrey and Hunter, J. Amer. Chem. Soc. 1912, 34, 702).

2-**Nitro-*p*-benzoquinone** $C_6H_3(NO_2)O_2$. The compound described by Friedländer (Ber. 1895, 28, 1387) is really 2-nitro- 3 or 6-*m*-nitro-*p*-hydroxyanilinoquinone (Kehrmann and Idzkowska, Ber. 1899, 32, 1066). The 2 : 6-**dichloro-** and 2 : 6-**chlorobromo-derivatives** of **nitroquinone** have been described (Guareschi and Daccomo, *ibid.* 1885, 18, 1171; Garzino, Atti R. Accad. Sci. Torino, 1890, 25, 250).

2 : 3-**Dicyano-*p*-benzoquinone** $C_6H_2(CN)_2O_2$. By oxidation of dicyanoquinol with the vapour of nitric acid (Thiele and Günther, Annalen, 1906, 349, 45).

The requisite dicyanoquinol is obtained by dissolving 2 kilos. of quinone in 60 litres of alcohol and 2·5 litres of concentrated sulphuric acid. A concentrated solution of potassium cyanide is added at ordinary temperature until the reaction is faintly alkaline: the solution shows a green fluorescence at this stage. The liquid is acidified, diluted with water and extracted with ether. The residue left after distilling off the ether is diluted with water and the dicyanoquinol precipitated as brownish leaflets. By recrystallising from water with addition of animal charcoal, feebly yellow coloured needles of the formula $C_6H_2(CN)_2(OH)_2+2H_2O$ are obtained (Bayer and Co., D. R. P. 117005, 1899; Thiele and Meisenheimer, Ber. 1900, 33, 675).

***p*-Benzoquinone-2-carboxylic acid**

$$C_6H_3(CO_2H)O_2$$

cannot apparently be isolated although the methyl and ethyl esters, which melt at 54° and 22° respectively, have been obtained by the oxidation of the corresponding esters of gentisic acid (Brunner, Monatsh. 1913, 34, 913). *Nitrososalicylic acid* is the 4-*oxime*. By adding acetic acid to a solution of potassium salicylate and sodium nitrite. Converted by ferric chloride to a green dyestuff (Bayer and Co., D. R. P. 48491, 1888). Also obtained by boiling 5-nitroso-N-methylanthranilic acid with aqueous sodium carbonate (Houben and Brassert, Ber. 1907, 40, 4739), m.p. 162°–163°. The *oxime-methylimine* $C_6H_3(:NOH)(:NCH_3)COOH$ has been obtained, (Houben, Brassert and Ettinger, *ibid.* 1909, 42, 2745).

***p*-Benzoquinone-2 : 3-dicarboxylic acid**

$$C_6H_2(CO_2H)_2O_2$$

The anhydride and imide have been prepared (Thiele and Günther, Annalen, 1906, 349, 45).

2-**Amino-*p*-benzoquinone** $C_6H_3(NH_2)O_2$. The *acetyl derivative,* m.p. 142°, is obtained by the oxidation of 2 : 4- or 3 : 4-diacetaminophenol (Kehrmann, Bahatrian and Gauhe, Ber. 1898, 31, 2400, 2304). Salts of 2-*amino*-p-*benzoquinone*-4-*imine* have been obtained by the oxidation of 2 : 4-diaminophenol (Kehrmann and Prager, *ibid.* 1906, 39, 3437). *Aminoquinone-diphenyldiimine* $C_6H_3(NH_2)(:N{\cdot}C_6H_5)_2$, m.p. 167°, results from the oxidation of neutral solutions of aniline salts by manganese or lead peroxide (Börnstein, *ibid.* 1901, 34, 1268). It yields azophenine on heating with aniline and its hydrochloride.

5-**Chloro-2-acetaminobenzoquinone,** m.p. 174°–175°.

5-**Bromo-2-acetaminobenzoquinone,** m.p. 183°–185°.

2-**Anilino-*p*-benzoquinone** $C_6H_3(NH{\cdot}C_6H_5)O_2$. By oxidation of anilino-quinol with N/10 ferric chloride (Willstätter and Majima, Ber. 1910, 43, 2588). The 4-phenylimine is obtained by adding sodium nitrite to 1-amino-2 : 4-dianilinobenzene in hydrochloric acid, m.p. 125° (O. Fischer and Heiler, *ibid.* 1893, 26, 385); 3 : 6- and 3 : 5-dichloro- and 3 : 5 : 6-trichloro-derivatives of anilinoquinone (Niemeyer, Annalen, 1885, 228, 332, 335, 337).

Many arylamino-quinones can be prepared by the general reaction.

$$2C_6H_4O_2+NH_2R=C_6H_3(NHR)O_2+C_6H_4(OH)_2$$

(Liebermann and Jacobson, Annalen, 1883, 221, 75; Zincke, Ber. 1881, 14, 1494). The greater the basicity of an amine the more readily it reacts with a quinone. Aniline and its homologues give mono- and di-arylamino derivatives simultaneously, whilst secondary amines and the nitro-anilines yield mono-derivatives. The weakest bases do not react with quinones in aqueous solution. The influence of solvents on the reaction has been studied by H. Suida and his co-workers (Annalen, 1918, 416, 113, 164, 181, 189), who have prepared a large number of derivatives. If an amino-phenolcarboxylic acid is used, mordant dyestuffs are obtained (von Heyden, D. R. P. 119863, 1898). Thus, for example, 19 kilos. of amino-salicylic acid are dissolved with 14 kilos. of sodium acetate in 300 kilos. of alcohol. A solution of 11 kilos. of benzoquinone in 300 kilos. of alcohol is added and the mixture boiled from 3 to 5 hours. Then 500 kilos. of alcohol are distilled off and 500 kilos. of water added to the residue. The precipitated colouring matter is repeatedly washed and made up as a paste or as sodium salt. The colouring matter gives a bright brown on wool, deep brown shades may be obtained on a chrome mordant which may be used before or after the dyeing operation.

In addition to benzoquinone, chloranil or β-naphthaquinone may be used; the acids employed are *o*- and *p*-aminosalicylic, *p*-amino-α

cresotinic, *p*-amino-*o*-cresolcarboxylic, amino-*α*-hydroxynaphthoic, amino-*β*-hydroxynaphthoic.

2 : 5-**Diamino-*p*-benzoquinone** $C_6H_2(NH_2)_2O_2$, decomposes at 325°–330°. It is obtained by hydrolysis of its *diacetyl derivative*, the oxidation product of 2 : 5-diacetaminophenol (Kehrmann and Betsch, Ber. 1897, 30, 2099). 6-*Chloro*-2 : 5-*diacetaminoquinone*, m.p. 225°–226° (Kehrmann and Tiesler, J. pr. Chem. 1889, ii. 40, 491). *Diimine* (Nietzki, Ber. 1887, 20, 2115).

Tetramethyl-2 : 5-diamino-*p*-benzoquinone

$$C_6H_2[N(CH_3)_2]_2O_2$$

From quinone or chloroquinone and dimethylamine (Mylius, Ber. 1885, 18, 467; Kehrmann, *ibid.* 1890, 23, 905).

Diethyl-2 : 5-diglycinoquinone

$$C_6H_2(NH{\cdot}CH_2{\cdot}CO_2C_2H_5)_2$$

m.p. 215°; *diethyl-2 : 5-dialaninoquinone*

$$C_6H_2[NH{\cdot}CH(CH_3){\cdot}CO_2C_2H_5]_2$$

m.p. 140° (E. Fischer and Schrader, Ber. 1910, 43, 525).

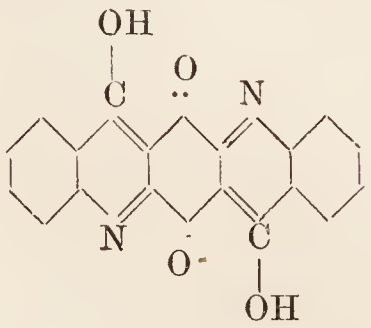
2-**Amino-5-anilino-*p*-benzoquinone**

$$C_6H_2(NH_2)(NH{\cdot}C_6H_4)O_2$$

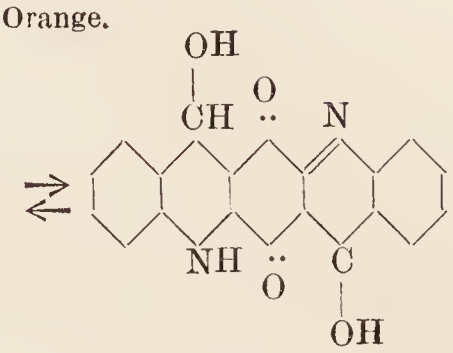
m.p. 280°–282° (Kehrmann and Bahatrian, Ber. 1898, 31, 2401).

Phenylimine $C_6H_2(NH)(NH{\cdot}C_6H_5)(:N{\cdot}C_6H_5)O$ (Majima, *ibid.* 1911, 44, 229).

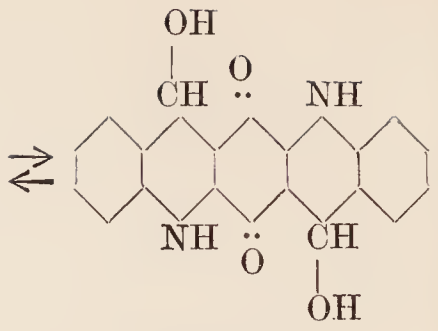
2 : 5-**Dianilino-*p*-benzoquinone** (*quinone-anilide*) $C_6H_2(NH{\cdot}C_6H_5)_2O_2$. From quinone and aniline (Hofmann, Jahresb. 1863, 415; Wichelhaus, Ber. 1872, 5, 851; Knapp and Schultz, Annalen, 1881, 210, 178) and by other reactions (Niemeyer, *ibid.* 1885, 228, 331; O. Fischer and Hepp, Ber. 1888, 11, 2618; Hebebrand and Zincke, *ibid.* 1883, 16, 1556; Willstätter and Majima, *ibid.* 1910, 43, 2588). Many other aromatic amines react similarly (*v. supra*). The dicarboxylic acid obtained from benzoquinone and anthranilic acid is condensed by concentrated sulphuric acid to 1 : 4 : 5-Triketo-acridine-3-*o*-aminobenzoic acid (Suchanek, J. pr. Chem. 1914, [ii], 90, 457). Further condensation leads to double ring condensation, quinone-diacridone being formed (Scharvin, J. Russ. Phys. Chem. Soc. 1915, 47, 1260). This substance is weakly basic and weakly acidic, it gives green and bluish-violet compounds on reduction with hyposulphite.



Orange.

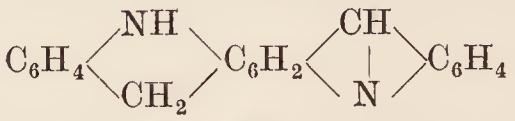


Green.



Bluish-violet.

On distillation with zinc-dust, dihydroquinacridine



is formed (Lesnianski, Ber. 1918, 51, 695).

The *monoimine* of *dianilino-p-benzoquinone* is obtained by oxidising aniline with sodium persulphate (Majima, *ibid.* 1911, 44, 229).

The *phenylimine* and the *diphenyldiimine* (*azophenine*) are of considerable interest as being intermediate compounds in the formation of indulines by heating hydroxy- and amino-azo-compounds with aniline.

2 : 5-**Dianilino-*p*-benzoquinone-phenylimine**

$$C_6H_2(\cdot NHC_6H_5)_2(:N{\cdot}C_6H_5) : O$$

is produced by heating 1 part of benzoquinone with 20 parts of glacial acetic acid and 2 parts of aniline (Zincke and Hagen, Ber. 1885, 18, 787); by long continued boiling of 2 parts of aniline with 1 part of *o*-nitrophenol and 10–20 parts of 50 p.c. acetic acid (O. Fischer and Hepp, Annalen, 1891, 262, 247); by heating *m*-hydroxydiphenylnitrosamine

$$HO{\cdot}C_6H_4{\cdot}N(NO){\cdot}C_6H_5$$

with aniline and its hydrochloride to 100° (Kohler, Ber. 1888, 21, 910; Fischer and Hepp, *ibid.* 675; Annalen, 1891, 262, 249); by warming quinone-phenylimine with 15–20 parts of aniline at 100° (Bandrowski, Monatsh. 1888, 9, 415); from 5-diazo-2-hydroxy-benzoic acid and aniline (Dierbach, Annalen, 1893, 273, 118); by warming aniline with hydrogen peroxide and dilute acetic acid (Schunck and Marchlewski, Ber. 1892, 25, 3574); by the action of hæmin on aniline (Küster, *ibid.* 1910, 43, 2962); accompanied by amino-anilino-quinone-phenylimine by oxidising aniline in aqueous acetic acid solution at 0° with sodium bromate (Majima, *ibid.* 1911, 44, 229); by the electrolytic reduction of *p*-nitrophenol in a mixture of 2 parts of aniline and 1 part of hydrochloric acid (sp.gr. 1·19) (Löb, Zeitsch. Elektrochem. 1900, 6, 441); and by the action of aniline on *o*-benzoquinone (Jackson and Koch, Ber. 1898, 31, 1457). M.p. 203°. Yields ethers of anilinohydroxyquinone-phenylimine when heated with alcohols and sulphuric acid, and azophenine on continued heating with aniline at 180°–200°. Nitrous acid yields several products, three of these melt at 209°, 248°, and 286° respectively (Istrati and Mihailescu, Bull. Acad. Sci. Roumaine, 1912/13, 1, 25).

2 : 5-**Dianilino-*p*-benzoquinone-diphenyldiimine** (*azophenine*) $C_6H_2(NH{\cdot}C_6H_5)_2(:N{\cdot}C_6H_5)_2$ is obtained by heating *p*-nitrosophenol with aniline salts (Kimich, Ber. 1875, 8, 1028; Witt and Thomas, Chem. Soc. Trans. 1883, 43, 115); by heating 2 parts of aminoazobenzene with 4

parts of aniline and 1 part of aniline hydrochloride for 24 hours to 80°–90° (Witt and Thomas; also Witt, Ber. 1887, 20, 1539), and by numerous other reactions (Witt, *ibid.* 1877, 10, 1311; O. Fischer and Hepp, *ibid.* 1887, 20, 2480; 1888, 21, 683, 686; Annalen, 1889, 255, 146; 1890, 256, 258; Ikuta, *ibid.* 1888, 243, 285; Szarvasy, Chem. Soc. Trans. 1900, 77, 207; Börnstein, Ber. 1901, 34, 1268).

Respecting the action of aniline on nitrosophenol, Cursan and Boord (Science, 1921, 53, 218) consider that quinone phenylhydrazone is first found which is converted into the tautomine benzeneazophenol if the reaction mixture is diluted or neutralised. Further action of aniline on the quinone phenylhydrazone gives successively monoanilinoquinone phenylhydrazone, dianilinoquinone and azophenine.

For the preparation of the substance, Fischer and Hepp recommend heating 100 grms. of nitrosodiphenylamine with 500 grms. of aniline and 100 grms. of aniline hydrochloride for 8–10 hours on the water-bath. The crystals which separate are washed successively with water, dilute alcohol and absolute alcohol and then recrystallised from toluene; m.p. 246°. Soluble in chloroform: the solution in concentrated sulphuric acid is violet and suddenly turns blue at 100°. Heated to 360°, azophenine yields aniline and fluorindine; heated with primary bases, indulines are produced. Water-soluble indulines are produced when *p*-phenylenediamine is employed (Dahl and Co., D. R. P. 43008, 1887), whilst bluish-grey water-soluble dyestuffs are formed by heating with hydrochlorides of nitrosodialkylanilines in glacial acetic acid solution (Farbw. Griesheim, D. R. P. 55229, 1890). By long-continued boiling with alcohol and sulphuric acid, aniline and dianilinoquinone are produced. Reduction gives tetraanilinobenzene (hydrazophenine), m.p. 173°–174° (Fischer and Hepp, Ber. 1887, 20, 2483). Several halogen derivatives have been prepared (Fischer and Hepp, Ikuta).

Methylazophenine $C_{31}H_{26}N_4$, from *p*-nitrosophenyltolylamine and aniline, melts at 230° (Reichold, Annalen, 1889, 255, 166).

3 : 5-**Di-methylphenylamino-*p*-benzoquinone**

$$C_6H_2[N(CH_3)(C_6H_5)]_2O_2$$

By warming an alcoholic solution of monomethylaniline with quinone. Red-brown leaflets with blue reflex (Möhlau and Redlich, Ber. 1911, 44, 3616).

Dianilino - chloro - *p* - benzoquinone. The phenylimine, $C_6HCl(NHC_6H_5)_2(:NC_6H_5):O$, m.p. 195°, is obtained by adding 5 molecular proportions of aniline to an alcoholic solution of trichloroquinone-chloroimine (Andresen, J. pr. Chem. 1883, ii. 28, 428).

3 : 6-**Dichloro**-2 : 5-**diamino-*p*-benzoquinone** (*chloranilimide*) $C_6Cl_2(NH_2)_2O_2$ is obtained by the action of ammonia on chloranil (Laurent, Berz. Jahresbericht, 25, 850; Knapp and Schultz, Annalen, 1881, 210, 184), or on the dimethyl ether of chloranilic acid (Kehrmann, J. pr. Chem. 1889, ii. 40, 371). Fine reddish-brown needles; sublimes. Insoluble in water, alcohol, ether and ammonia; dissolves in alcoholic potash with a violet-red colour and on boiling with caustic potash solution gives ammonia and chloranilic acid.

3 : 6-**Dichloro**-2 : 5-**dianilino-*p*-benzoquinone** (*chloranilanilide*) $C_6Cl_2(NHC_6H_5)_2O_2$, results from the action of aniline on chloranil (Hesse, Annalen, 1860, 114, 306; Hofmann, Jahresb. 1863, 415; Knapp and Schultz, Annalen, 1881, 210, 187), and by other reactions (Schmitt and Andresen, J. pr. Chem. 1881, ii. 24, 431; Andresen, *ibid.* 1883, ii. 28, 427; Niemeyer, Annalen, 1885, 228, 333). Yellowish-brown metallic tablets, m.p. 285°–290°, sublimes with very little decomposition. The *diphenylimine* (*dichloroazophenine*) has been described by Bandrowski and Prokopeczko (Bull. Acad. Sci. Cracow, 1901, 441).

Other derivatives of quinone containing groups ·NHR and ·NR_2 in positions 2 and 5 are described by Schmitt and Andresen; Ville and Astre (Bull. Soc. chim. 1895, iii. 13, 746; 1896, iii. 15, 1027, 1033); Jackson and Torrey (Ber. 1897, 30, 531; Amer. Chem. J. 1898, 20, 419); Imbert and Pagès (Bull. Soc. chim. 1898, iii. 19, 575).

3 : 6-**Dinitro**-2 : 5-**diamino-*p*-benzoquinone**

$$C_6(NO_2)_2(NH_2)_2O_2$$

is obtained by adding the nitrate of diaminoquinone-diimine to 15–20 parts of concentrated sulphuric acid at a temperature below 10°. Dark yellow needles, gives tetraaminoquinol on reduction (Nietzki, Ber. 1887, 20, 2115).

3-**Nitro**-2 : 5-**dianilino-*p*-benzoquinone**

$$C_6H(NO_2)(NHC_6H_5)_2O_2$$

(Kehrmann and Idzkowska, Ber. 1899, 32, 1067).

α- and *β*- **Dinaphthylamino-*p*-benzoquinones** $C_6H_2O_2(NHC_{10}H_7)_2$, and the dichloro-compounds $C_6Cl_2O_2(NHC_{10}H_7)_2$, when heated in high boiling solvents give highly coloured compounds which are of technical use after sulphonation (Meister, Lucius and Brüning, D. R. P. 253091, 1911. See other patents of the same firm, viz. D. R. PP. 253761, 255642, 257884, 262180, 263352, 270885, all of 1911, and 265195, 265196, 270401 of 1912).

2 : 6-**Diamino-*p*-benzoquinone** $C_6H_2(NH_2)_2O_2$ and the hydrochloride of its 4-*imine* are obtained by the oxidation of 1 : 2 : 3 : 5-tetraaminobenzene with ferric chloride (Nietzki and Hagenbach, Ber. 1897, 30, 542). The *diacetyl-derivative*, m.p. 265°–270°, by oxidising triacetaminophenol (Bamberger, Ber. 1883, 16, 2402) or tetraacetyldiaminoquinol (Nietzki and Preusser, *ibid.* 1886, 19, 2247; 1896, 29, 797). *Diphthalyl derivative*, m.p. 277° (Piutti, Gazz. chim. ital. 1886, 16, 254).

Triamino-*p*-benzoquinone $C_6H(NH_2)_3O_2$. By drawing air through a solution of pentaaminobenzene hydrochloride (1 grm.) and sodium acetate (2 grms.) in water (150 c.c.) for 2 days. Dark brown, insoluble, easily decomposable powder (Jackson and Grindley, Ber. 1893, 26, 2305).

Hydroxyquinones. The hydroxyquinones are of considerable theoretical interest and in the naphthalene and anthracene series acquire considerable importance as dyestuffs.

2-**Hydroxy-*p*-benzoquinone** $C_6H_3(OH)O_2$. By oxidising 1 : 2 : 4-trihydroxybenzene in absolute ethereal solution with silver oxide. Crystallises in yellow rectangular tablets. Turns brown at 120°, black at 124°, but does not melt. Liberates iodine from hydriodic acid, easily reduced to

trihydroxybenzene with which a quinhydrone can be obtained (R. Willstätter and F. Müller, Ber. 1911, 44, 2181).

Compounds of apparently the same empirical formula have been described as ' melanic ' acids. They result by boiling tannin with caustic potash or by oxidising solutions of salicylaldehyde or quinone (Büchner, Annalen, 1845, 53, 373 ; Piria, *ibid.* 1841, 39, 167 ; Woskresensky, J. pr. Chem. 1845, 34, 251).

Nitrosoresorcinol (Fèvre, Bull. Soc. chim. 1883, 39, 585) and dinitrosoresorcinol (Fitz, Ber. 1875, 8, 631) can, in the tautomeric forms

$C_6H_3(OH)(:NOH):O$ and $C_6H_2(NO)(OH)(:NOH):O$

be regarded as the *monoximes* of *hydroxyquinone* and *nitrosohydroxyquinone* respectively (*see* also Kostanecki, Ber. 1887, 20, 3133).

Mononitrosoresorcinol has been used in the preparation of oxazine dyestuffs (resorcin blue), which proved to be of little technical value (Bindschedler and Busch, D. R. P. 14622, 1880).

Dinitrosoresorcinol is used as a paste under the names of ' fast green ' and ' solid green ' on silk or cotton mordanted with iron. A method for directly colouring the fibre with lakes of quinone-oximes is to impregnate the material with a phenol (*e.g.* resorcinol), a mordant (ferrous, chromium or cobalt salt) and an acid, then to dry and subsequently pass the goods through a boiling neutral nitrite solution (Kalle and Co., D. R. P. 99486, 1897 ; 101523, 1898).

Dinitrosoresorcinol gives a fast brown dyestuff, *essacine*, when acted on by sodium hyposulphite ($NaHSO_2$) (Kendall, D. R. P. 54615). A different colouring matter is produced when it is reduced with sodium hydrogen sulphite (Binder, D. R. P. 65049, 1891).

A derivative of hydroxyquinone is *chrysone* $C_{15}H_8O_5$, obtained by oxidation of chrysin. Gives colour reactions of anthocyanin (M. Nierenstein, Ber. 1912, **45**, 499).

2-Methoxy-*p*-benzoquinone $C_6H_2(OCH_3)O_2$. By oxidation of *o*-anisidine (Mühlhäuser, Annalen, 1881, 207, 251 ; Will, Ber. 1888, 21, 605) ; the dimethyl ether of *p*-aminoresorcinol (Bechhold, Ber. 1889, 22, 2381) ; or 3-methoxy-4-aminophenol (Henrich and Rhodius, *ibid.* 1902, 35, 1486), m.p. 140°. *Monoxime* (nitrosoguaiacol) several derivatives (Bridge and Morgan, Amer. Chem. J. 1899, 22, 486). *Dioxime*, m.p. 250° (Best, Annalen, 1889, 255, 187 ; Pfob, Monatsh. 1897, 18, 473).

2-Methylthiol-*p*-benzoquinone $C_6H_3(SCH_3)O_2$. Red needles, m.p. 148°. By oxidation of 4-amino-3-methylthiolphenol, chloranil is formed when treated with chlorine in chloroform solution. Aniline gives 2 : 5-dianilino-*p*-benzoquinone with elimination of methyl mercaptan (Zincke and Müller, Ber. 1913, 46, 1777).

2-Ethoxy-*p*-benzoquinone $C_6H_3(OC_2H_5)O_2$, m.p. 117° (Will and Pukall, Ber. 1887, 20, 1132 ; Kietaibl, Monatsh. 1898, 19, 552).

Trichlorohydroxy-*p*-benzoquinone

$C_6Cl_3(OH)O_2$

m.p. 194°, yields chloranilic acid when warmed with alkalis (Zincke and Schaum, Ber. 1894, 27, 556).

Tribromohydroxy-*p*-benzoquinone

$C_6Br_3(OH)O_2$

m.p. 205°. By hydrolysis of the hemiacetal $C_6Br_3(OH)O(OCH_3)_2$ (Jackson and Flint, Amer. Chem. J. 1908, 39, 80). The ' tribromoxyhydrochinon,' m.p. 206°–207°, obtained by the action of bromine on 1 : 2 : 4-trihydroxybenzene is probably identical (Barth and Schreder, Monatsh. 1884, 5, 593).

5-Amino-2-hydroxy-*p*-benzoquinone

$C_6H_2(NH_2)(OH)O_2$

The *monoimine* is identical with diiminoresorcin ; *acetyl derivative* $C_6H_2(NHCOCH_3)(OH)O_2$, m.p. 170° (Nietzki and Schmidt, Ber. 1889, 22, 1657 ; Kehrmann and Betsch, *ibid.* 1897, 30, 2102).

5-Dimethylamino-2-hydroxy-*p*-benzoquinone $C_6H_2[N(CH_3)_2][OH]O_2$. Red crystals (Kehrmann, Ber. 1890, 23, 906).

5-Anilino-2-hydroxy-*p*-benzoquinone

$C_6H_2(NHC_6H_5)(OH)O_2$

and several derivatives (Zincke and Hagen, Ber. 1885, 18, 788). Melts and decomposes at 228°–230° (Kehrmann and Bahatrian, *ibid.* 1898, 31, 2401).

For other derivatives of 5-amino-2-hydroxyquinone, *see* Fischer and Hepp (Ber. 1888, 21, 677) ; Kehrmann (*ibid.* 1890, 23, 900) ; Jackson and Torrey (*ibid.* 1897, 30, 529 ; Amer. Chem. J. 1898, 20, 410). Ethers of the type

$C_6Cl(OC_2H_5)(NRR')_2O_2$

have been prepared by Kehrmann (J. pr. Chem. 1891, ii. 43, 261).

2 : 5-Dihydroxy-*p*-benzoquinone

$C_6H_2(OH)_2O_2$

is obtained by elimination of carbon dioxide from dihydroxyquinonedicarboxylic acid

$C_6(OH)_2(CO_2H)_2O_2$

and by oxidation of 1 : 2 : 4 : 5-tetrahydroxybenzene with ferric chloride (Löwy, Ber. 1886, 19, 2387). Also by heating diiminoresorcinol with 10 parts of 10 p.c. caustic potash at 70° (Nietzki and Schmidt, *ibid.* 1888, 21, 2374 ; 1889, 22, 1654) and by heating anilinohydroxyquinone or its anilide or tetramethyldiaminoquinone with dilute alkalis. It can be obtained from dianilino-quinone or chloro-dianilinoquinone by heating with a mixture of 3 parts of concentrated sulphuric acid and 2 parts of alcohol (Kehrmann, Ber. 1890, 903) ; together with methyl-*o*-aminophenol by heating N-methylphenoxazine-*o*-quinone with sodium hydroxide solution (Diepolder, *ibid.* 1899, 32, 3523) ; by heating 2-amino-5-anilinoquinone with caustic soda or dilute sulphuric acid (Kehrmann and Bahatrian, *ibid.* 1898, 31, 2402) and by alkaline hydrolysis of the diethyl ether (Knoevenagel and Bückel, *ibid.* 1901, 34, 2402). Melts and partially decomposes at 215°–220°.

Strong acid giving highly coloured salts ; stannous chloride reduces to tetrahydroxybenzene. Bromine and caustic soda give bromanilic acid ; nitric acid gives nitranilic acid. The compound $C_6H_6O_4N_2$ obtained with hydroxylamine and formulated by Nietzki and Schmidt (Ber. 1888, 21, 2377) as a dioxime, is really hydroxylaminohydroxyquinone-monoxime as it gives 4 : 6-diaminoresorcinol on reduction (Kehrmann and Betsch, *ibid.* 1897, 30, 2097). Reacts tautomerically as 4 : 5-dihydroxy-*o*-quinone, with *o*-phenylenediamine, dihydro-

phenazine is produced. 2 : 5-Dihydroxy-quinone apparently gives two series of ethers,

$$C_6H_2(OAlkyl)_2O_2$$

Dimethyl ethers (Hofmann, Ber. 1878, 11, 332; Will, *ibid.* 1888, 21, 608; Nietzki and Schmidt, *ibid.* 2376; Nietzki and Rechberg, *ibid.* 1890, 23, 1216; Ciamician and Silber, *ibid.* 1893, 26, 786; Knoevenagel and Bückel, *ibid.* 1901, 34, 3996). *Diethyl ethers* (Nietzki and Rechberg, Knoevenagel and Bückel). *Dipropyl ether*, m.p. 187°, and *dibenzoyl derivative*, m.p. 174° (Knoevenagel and Bückel).

6-**Chloro**-2 : 5-**dihydroxy**-*p*-**benzoquinone**

$$C_6HCl(OH)_2O_2$$

melts and decomposes at 240° (Kehrmann and Tiesler, J. pr. Chem. 1889, ii. 40, 484).

6-**Chloro**-2 : 5-**diphenoxy**-*p*-**benzoquinone**

$$C_6HCl(OC_6H_5)_2O_2$$

m.p. 169°–170° (Jackson and Grindley, Amer. Chem. J. 1895, 17, 655).

3 : 6-**Dichloro**-2 : 5-**dihydroxy**-*p*-**benzoquinone** (*chloranilic acid*) $C_6Cl_2(OH)_2O_2+2H_2O$. By the action of potassium hydroxide on chloranil (Erdmann, Annalen, 1843, 48, 315) or trichloroquinone (Graebe, *ibid.* 1868, 146, 24)

$$C_6Cl_4O_2+4KOH=C_6Cl_2(OK)_2O_2+2KCl+2H_2O$$

$$2C_6HCl_3O_2+3KOH$$
$$=C_6Cl_2(OK)_2O_2+KCl+C_6HCl_3(OH)_2+H_2O$$

Preparation.—10 parts of chloranil are moistened with alcohol and added to a solution of 9 grms. of sodium hydroxide in 210 grms. of water at 70°–80°. After 2 hours, 20 grms. of sodium chloride are added, the sodium chloranilate is washed with 10 p.c. brine, dissolved in boiling water and precipitated with hydrochloric acid (Stenhouse, Annalen Spl., 1872, 8, 14; Graebe, Annalen, 1891, 263, 24). Loses water of crystallisation at 115°; melts in sealed tube at 283°–284° (Michael, Ber. 1895, 28, 1631). 100 parts water dissolve 0·19 acid at 13·5°, 1·4 parts at 99°. Solutions are violet-red. Strong acid; electric conductivity, Barth (*ibid.* 1892, 25, 837); Coffetti (Gazz. chim. ital. 1900, 30, ii. 238); Fiorini (*ibid.* 1901, 31, i. 35). Armstrong has suggested that the chloroanilates are derived from 4 : 5-dihydroxy-1 : 2-benzoquinone (Chem. Soc. Proc. 1893, 9, 57). Molecular heat of combustion at constant pressure, 486·2 cal. (Valeur, Ann. Chim. 1903, vii. 29, 507). Several reactions lead to compounds of the aliphatic series, *e.g.* nitric acid gives chlorpicrin and oxalic acid; iodine in alkaline solution gives iodoform (Jackson and Torrey, Amer. Chem. J. 1898, 20, 429).

The salts of the alkali metals dissolve in water with intense violet colour; most of the other salts are coloured precipitates (Hesse, Annalen, 1860, 114, 304; Stenhouse; Graebe; Erdmann; Pope (Chem. Soc. Trans. 1892, 61, 585); Jackson and Torrey).

α-Dimethyl ether $C_6Cl_2(OCH_3)_2O_2$, m.p. 141°–142°. From silver chloranilate and methyl iodide. This compound and an isomer, m.p. 157°–158° (*β-dimethyl ether*) are obtained by the action of methyl alcoholic potash on chloranil in the cold. The α-dimethyl ether unites directly with sodium methoxide, giving the sodium salt of *dichlorodimethoxy-quinone-dimethylhemiacetal* $(CH_3O)_2C_6Cl_2(OH)_2(OCH_3)_2$ (Jackson and Grindley, Amer. Chem. J. 1895, 17, 600). Several derivatives have been prepared (Jackson and Oenslager and Torrey, *ibid.* 1896, 18, 7; 1898, 20, 429).

α-Diethyl ether, m.p. 104°–105°; *β-diethyl ether*, m.p. 97°–98° (Stenhouse; Kehrmann, J. pr. Chem. 1889, ii. 39, 318; 1889, ii. 40, 367; Jackson and Torrey).

Dibenzyl ether, m.p. 142° (Jackson and Oenslager).

Diphenyl ether, m.p. 243° (Jackson and Grindley).

Diacetyl derivative $C_6Cl_2(OCOCH_3)_2O_2$, m.p. 182·5° (Nep, J. pr. Chem. 1890, ii. 42, 170).

Biscyanimide

$$CN_2 : C<\begin{matrix}CCl : C(OK)\\C(OK) : CCl\end{matrix}>C : N_2C+2H_2O$$

From potash and cyanamide on chloranil in boiling aqueous suspension (Imbert, Compt. rend. 1898, 126, 1879).

3 : 6-**Dichloro**-2-**amino**-5-**hydroxy**-*p* **benzoquinone** $C_6Cl_2(NH_2)(OH)O_2$, obtained as ammonium salt by solution of chloranil in dilute aqueous ammonia (Erdmann, Annalen, 1843, 48, 321; Laurent, Berz. Jahresbericht, 25, 849).

3 : 6-**Dibromo**-2 : 5-**dihydroxy**-*p*-**benzoquinone** (*bromanilic acid*) $C_6Br_2(OH)_2O_2$. Preparation and properties resemble those of chloranilic acid (Stenhouse, Annalen, 1854, 91, 311; Sarauw, *ibid.* 1881, 209, 115; Hantzsch, Ber. 1887, 20, 1303; Salzmann, *ibid.* 1997; Hantzsch and Schniter, *ibid.* 2040; *ibid.* 1888, 21, 2438; Graebe and Weltner, Annalen, 1891, 263, 35; Levy and Jedlicka, *ibid.* 1889, 249, 81; Landolt, Ber. 1892, 25, 852; Ling, Chem. Soc. Trans. 1892, 61, 574; Pope, *ibid.* 586; Coffetti, Gazz. chim. ital. 1900, 30, ii. 238; Fiorini, *ibid.* 1901, 31, i. 35; Descomps, Bull. Soc. chim. 1899, iii. 21, 368). *Diethyl ether* $C_6Br_2(OC_2H_5)_2$, m.p. 139° (Bentley, Amer. Chem. J. 1898, 20, 479). *Dimethylhemiacetal* of *dimethyl ether*

$$(CH_3O)_2C_6Br_2(OH)_2(OCH_3)_2$$

m.p. 178°–188° (Jackson and Grindley, *ibid.* 1895, 17, 652). *Diphenyl ether* $C_6Br_2(OC_6H_5)_2O_2$, m.p. 266°–267° (Jackson and Grindley).

Biscyanimide $CN_2 : C_6Br_2(OK)_2 : N_2C$ (Imbert, Compt. rend. 1898, 126, 529).

3 : 6-**Dibromo**-2 : 5-**diamino**-*p*-**benzoquinone** (*bromanilamide*), from bromanil and alcoholic ammonia (Stenhouse).

3 : 6-**Dibromo**-2 : 5-**dianilino**-*p*-**benzoquinone** (Stenhouse, Annalen, 1872, Spl. 8, 22; van Erp, Rec. trav. chim. 1911, 30, 270).

3 : 6-**Dibromo**-2 : 5-**amino**-5-**hydroxy**-*p*-**benzoquinone** $C_6Br_2(NH_2)(OH)O_2$, from bromanil and aqueous ammonia (Stenhouse, *ibid.* 1854, 91, 313).

3-**Chloro**-6-**bromo**-2 : 5-**dihydroxy**-*p*-**benzoquinone** $C_6ClBr(OH)_2O_2+H_2O$ (Levy, Ber. 1885, 18, 2370; Levy and Schultz, Annalen, 1881, 210, 163; Ling, Chem. Soc. Trans. 1887, 51, 785; Hantzsch, Ber. 1889, 22, 2829; Kehrmann and Tiesler, J. pr. Chem. 1889, ii. 40, 486; Pope, Chem. Soc. Trans. 1892, 61, 584; Ling and Baker, *ibid.* 591).

3-**Chloro**-6-**iodo**-2 : 5-**dihydroxy**-*p*-**benzoquinone** $C_6ClI(OH)_2O_2$. Explodes at 275°. Prepared by adding the theoretical amount of iodine dissolved in sodium hydroxide to an acidified solution of 6-chloro-2 : 5-dihydroxy-

quinone (Kehrmann and Tiesler, J. pr. Chem. 1889, ii. 40, 487).

3 : 6-**Dicyano-2 : 5-dihydroxy-*p*-benzoquinone** (*cyanilic acid*). The potassium salt, $C_8O_4N_2K_2$, is obtained by the reaction of chloranil and potassium cyanide in methyl alcohol solution. Strong acid, stable towards reducing and hydrolytic agents. The salts are fluorescent (M. M. Richter, Ber. 1911, 44, 3469).

3-**Nitro-2 : 5-dihydroxy-*p*-benzoquinone**

$$C_6H(NO_2)(OH)_2O_2$$

By warming nitrodiiminoresorcinol with 10–15 parts of 10 p.c. solution of potassium hydroxide (Nietzki and Schmidt, Ber. 1889, 22, 1661). Golden yellow needles. For reactions compare also Kehrmann and Idzkowska (*ibid.* 1899, 32, 1071).

3 : 6-**Dinitro-2 : 5-dihydroxy-*p*-benzoquinone** (*nitranilic acid*) $C_6(NO_2)_2(OH)_2O_2$. By leading nitrous fumes into a well-cooled ethereal solution of quinol, a few drops of water being added towards the end of the reaction (Nietzki, Annalen, 1882, 215, 138); by the action of fuming nitric acid on quinol-dicarboxylic acid (Herrmann, *ibid.* 1882, 211, 342); by the action of nitric acid (generally mixed either with acetic or sulphuric acid) on dinitroquinol (Nietzki); quinol diacetate (Nietzki and Benckisser, Ber. 1885, 18, 499; *cf.* Nietzki, *ibid.* 1883, 16, 2093); dihydroxyquinonedicarboxylic acid (Hantzsch, *ibid.* 1886, 19, 2399), and on the triacetyl- and nitro- derivatives of 1 : 2 : 4-trihydroxybenzene (Thiele and Jäger, *ibid.* 1901, 34, 2838). It is also obtained by warming dinitro-diaminoquinone with dilute alkali (Nietzki and Benckisser, *ibid.* 1887, 20, 2116), and by the action of concentrated solution of sodium nitrite on chloranil (Nef, *ibid.* 1887, 20, 2028; Amer. Chem. J. 1889, 11, 17).

For the preparation of nitranilic acid, Nietzki and Benckisser recommend the solution of quinol diacetate in 6 parts of nitric acid (sp.gr. 1·48–1·50) at 10°, then cooling to −8° and adding 6 parts of concentrated sulphuric acid previously cooled to the same temperature. After standing some hours at −3° to 0°, the mixture is poured on to 12 to 15 parts of crushed ice, rapidly filtered and dissolved in potassium hydroxide solution. The potassium salt separates, is collected after 12 hours and recrystallised from hot water containing caustic potash. Nietzki (Ber. 1910, 43, 3457) states that potassium nitranilate is obtained in 75–80 p.c. yield by making a paste of quinol, acetic anhydride and a few drops of concentrated sulphuric acid and adding this to cold nitric acid (sp.gr. 1·48). Concentrated sulphuric acid is then poured in, the mixture is kept at 0° for 12 hours, poured on to ice and the solid product treated with ice and caustic potash (*see* also Henle, Annalen, 1906, 350, 334).

Nitranilic acid melts in its water of crystallisation, the anhydrous acid explodes at 170° without previous fusion. It is a strong acid, salts (Nef, Ber. 1887, 20, 2028; also Muthmann, *ibid.*). Electrical conductivity (Barth, Ber. 1892, 25, 837; Coffetti, Gazz. chim. ital. 1900, 30, ii. 237).

A compound $C_{12}H_6O_{10}N_2$ obtained by the action of nitrous acid on an ethereal solution of quinone has been formulated as an addition-product of quinone and nitranilic acid (J. Schmidt, Ber. 1900, 33, 3249).

Diamino-dihydroxy-*p*-benzoquinone

$$C_6(NH_2)_2(OH)_2O_2$$

By oxidation of diaminotetrahydroxybenzene. Red brown needles; gives tetrahydroxyquinone when boiled with hydrochloric acid (Nietzki and Schmidt, Ber. 1885, 18, 1850).

Chloro-anilino-hydroxyethoxy-*p*-benzoquinone $C_6Cl(NHC_6H_5)(OH)(OC_2H_5)O_2$, m.p. 180° (Kehrmann, J. pr. Chem. 1891, ii. 43, 266).

Nitro-amino-dihydroxy-*p*-benzoquinone

$$C_6(NO_2)(NH_2)(OH)_2O_2$$

By oxidising nitroaminotetrahydroxybenzene (Nietzki and Benckisser, Ber. 1885, 18, 500).

Chlorodihydroxy-*p*-benzoquinone-sulphonic acid $C_6Cl(OH)_2(SO_3H)O_2$. The salt

$$C_6Cl(OH)_2(SO_3K)O_2+2H_2O$$

(red needles) is obtained from the potassium salt of trichloroquinolsulphonic acid (Graebe, Annalen, 1868, 146, 55).

Dihydroxy-*p*-benzoquinone-disulphonic acid $C_6(OH)_2(SO_3H)_2O_2$, also known as euthiocronic acid, is obtained from thiocronic acid, the product of the action of potassium hydrogen sulphite on chloranil (Hesse, Annalen, 1860, 114, 318; Greiff, Jahresb. 1863, 392; Graebe, Annalen, 1868, 146, 46).

Trihydroxy-*p*-benzoquinone $C_6H(OH)_3O_2$, its *triacetyl-*, *tribenzoyl-* and *monobromo- derivatives* have been described (Merz and Zetter, Ber. 1879, 12, 2040).

6-**Chloro-3-ethoxy-2 : 5-dihydroxy-*p*-benzoquinone** $C_6Cl(OC_2H_5)(OH)_2O_2$, m.p. 168°–170° (Kehrmann, J. pr. Chem. 1891, ii. 43, 265).

Tetrahydroxy-*p*-benzoquinone $C_6(OH)_4O_2$ results on exposing an aqueous solution of hexahydroxybenzene to the air (Lerch, Annalen, 1862, 124, 28), the sodium salt separates when air is passed for not too long a period through a solution containing hexahydroxybenzene and sodium carbonate (Nietzki and Benckisser, Ber. 1885, 18, 507, 1837). It is also formed when inosite is boiled with 4 to 5 parts of concentrated nitric acid (Maquenne, Ann. Chim. 1887, vi. 12, 112). Blue-black crystals, strong dibasic acid giving coloured salts; heated with acetyl chloride and zinc gives hexacetoxybenzene; nitric acid oxidises it to triquinoyl. *Diacetyl derivative*, m.p. 205° (Nietzki and Kehrmann, Ber. 1887, 20, 3152); *tetrabenzoyl derivative* (N. and K.; Maquenne, *l.c.*); phenylimine (Nietzki and Schmidt, Ber. 1888, 21, 1854). For *ethers* and *thio-ethers*, *see* Jackson and Grindley (Amer. Chem. J. 1895, 17, 579, 633) and Grindley and Sammis (*ibid.* 1897, 19, 290).

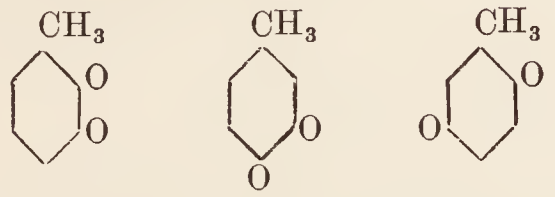
Benzene-diquinone $C_6O_4H_2$ is unknown: its dihydroxy-derivative is

Rhodizonic acid $\begin{matrix}CO\cdot CO\cdot C\cdot OH\\ \cdot \quad\quad \cdot \\ CO\cdot CO\cdot C\cdot OH\end{matrix}$. Rhodizonic acid was first obtained from the black mass obtained in Brunner's method for the manufacture of potassium, the salt $C_6(OK)_6$ is contained therein (Heller, Annalen, 1837, 24, 1; 1840, 34, 232; 1862, 124, 32; Will. *ibid.* 1861, 118, 189). Also produced from triquinoyl by warming with sulphurous acid to 40°–50°; the salt $C_6O_6Na_2$ separates on saturation with

sodium carbonate (Nietzki and Benckisser, Ber. 1885, 18, 513). Rhodizonic acid in the free state is colourless, crystalline and very unstable, oxidised by chlorine or dilute nitric acid to leuconic acid ($C_5H_8O_9$ or $C_5O_5,4H_2O$); a solution with sodium carbonate evaporated in the air gives croconic acid. The alkaline salts give intense reddish-yellow solutions which turn yellow on adding excess of alkali owing to the formation of salts of hydrocroconic acid. Astre has prepared salts $K_2C_6O_6$ and KHC_6O_6 from quinone and quinol by oxidation of alkaline solutions with air (Bull. Soc. chim. 1896, iii. 15, 460).

Benzene-triquinone or **triquinoyl** $C_6O_6,8H_2O$ has been obtained by acting on hexahydroxybenzene, tetrahydroxyquinone and rhodizonic acid with chlorine or nitric acid (Lerch, Annalen, 1862, 124, 34), and by the action of moderately concentrated nitric acid on 1 : 4-diaminotetrahydroxybenzene, diiminodihydroxyquinone or hexahydroxybenzene. Nietzki and Benckisser (Ber. 1885, 18, 504, 1842; *see* also Nietzki and Schmidt, *ibid.* 1888, 21, 1854) recommend the use of the above diamino- compound which is obtained by the reduction of nitranilic acid. Triquinoyl forms microscopic needles, melts about 95°, giving off carbon dioxide, insoluble in cold water, alcohol and ether. Liberates iodine from hydriodic acid, reduced by sulphurous acid to rhodizonic acid and by acid solution of stannous chloride to hexahydroxybenzene.

Toluquinones $C_7H_6O_2$. All three (two ortho and one para) toluquinones have been obtained; they will be referred to as



2 : 3 3 : 4 2 : 5

2 : 3-toluquinone, &c. Obtained by oxidation of dihydric phenols $C_6H_3(CH_3)(OH)_2$.

2 : 3-**Toluquinone.** Dark red prisms and needles, polymerises in ethereal solution to a bimolecular form, m.p. 194°–195° (Willstätter and F. Müller, Ber. 1911, 44, 2178). *Dioxime* $C_6H_3(CH_3)(:NOH)_2$, m.p. 140°; loss of water gives 1 : 2 : 3-toluylenefurazan, $C_6H_4\ll^{N}_{N}>O$, m.p. 44° (Zincke and Schwarz, Annalen, 1899, 307, 46).

5-**Amino**-2:3-**toluquinone** $C_6H_2(CH_3)(NH_2)O_2$. The hydrochloride of the 3-*imine*

$$C_6H_2(CH_3)(NH_2)(:NH,HCl):O$$

is obtained by adding excess of ferric chloride to a solution of diaminocresol dihydrochloride, saturated with sodium chloride. The dark red salt separates out at ordinary temperatures (Piccard, Ber. 1909, 42, 4332).

3 : 4-**Toluquinone.** From homocatechol in ethereal solution with silver oxide. Usually separates on rapidly evaporating the solvent as yellow mixed crystals, m.p. 65°–67°; on recrystallisation the dark red form, m.p. 80°–84°, is obtained. More stable than *o*-benzoquinone; polymerises to $(C_7H_6O_2)_2$, m.p. 124°–125° (Willstätter and F. Müller, Ber. 1911, 44, 2175; MacPherson and Boord, J. Amer. Chem. Soc. 1911, 33, 1525).

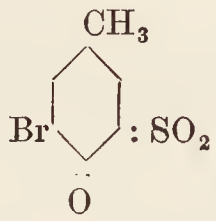
Dioxime, m.p. 128°; 1 : 3 : 4-*toluylenefurazane,* m.p. 37° (Zincke and Schwarz, Annalen, 1899, 307, 43; Green and Rowe, Chem. Soc. Trans. 1913, 101, 2452).

2 : 5 : 6-**Trichloro**-3 : 4-**toluquinone**

$$C_6(CH_3)Cl_3O_2$$

m.p. 97°–98° (Cousin, Ann. Chim. 1898, [vii.] 13, 532) or 103° (Bergmann and Francke, Annalen, 1897, 296, 163).

5-**Bromo**-3 : 4-**toluquinone.** A quino-sulphone of the constitution



has been obtained in polymeric (colourless) form by abstracting the elements of hydrogen chloride from the sulphochloride

$$C_6H_2Br(CH_3)(OH)(SO_2Cl)$$

(Zincke and Kempf, Ber. 1911, 44, 419).

2 : 5 : 6-**Tribromo**-3 : 4-**toluquinone,** m.p. 117°–118° (Cousin).

5-**Hydroxy**-3 : 4-**toluquinone.** Nitrosoorcinol $C_6H_2(CH_3)(NO)(OH)_2$ or

$$C_6H_2(CH_3)(OH)(:NOH)O$$

is the 4-oxime. *Dibenzoyl derivative,* m.p. 157°–158° (Henrich, Monatsh. 1897, 18, 169).

2 : 5-**Toluquinone.** By oxidation of 2 : 5-toluylenediamine (Nietzki, Ber. 1877, 10, 833) or *o*-toluidine (Ladenburg, *ibid.* 1128; Clark, Amer. Chem. J. 1892, 14, 565; Schniter, Ber. 1887, 20, 2283; Nietzki, Annalen, 1882, 215, 158). By electro-oxidation of 2-cresol and 3-cresol (Fichter and Ackermann, Helv. Chim. Acta, 1919, 2, 583; m.p. 68°–69°. Molecular heat of combustion at constant pressure, 805·3 cal. (Valeur, Compt. rend. 1897, 125, 872).

Resembles *p*-benzoquinone in most properties. On standing 24 hours with 2½ parts of sulphuric acid and 2½ parts of water, polymerises to 'isotoluquinone' $(C_7H_6O)_2$ (Spica, Gazz. chim. ital. 1882, 12, 225). Yields the triacetyl derivative of 2 : 4 : 5-trihydroxytoluene when heated with acetic anhydride and sulphuric acid (Thiele and Winter, Annalen, 1900, 311, 349).

Dichloride $C_7H_6Cl_2O_2$, m.p. 135°–136° (Clark); *dibromide,* m.p. 61°–62° (Clark).

Chloroimine $C_6H_3(CH_3)(:NCl)O$, m.p. 87°–88° from 5-amino-*o*-cresol (Hirsch, Ber. 1885, 18, 1514). *Chloroimine* from 6-amino-*m*-cresol, m.p. 75° (Städel and Kolb, Annalen, 1890, 259, 218).

Dimethylaminophenylimine

$$O:C_6H_3(CH_3):N\cdot C_6H_4\cdot N(CH_3)_2$$

(i.) From *o*-cresol and dimethyl-*p*-phenylenediamine, m.p. 123°; (ii.) from *m*-cresol, m.p. 117°–118° (Bayrac, Bull. Soc. chim. 1894, iii. 11, 1133; Dufet, Zeitsch. Kryst. 1897, 27, 631).

2 : 5-**Toluquinone-di-***p***-tolyldiimine**

$$CH_3\cdot C_6H_3(:N\cdot C_6H_4\cdot CH_3)_2$$

By acting on an alcoholic solution of di-*p*-tolyl-

2 : 5-toluylenediamine with concentrated ammoniacal copper nitrate. Orange-red needles, m.p. 145°–146°; dissolves with bright blue colour in concentrated sulphuric acid (Green, Ber. 1893, 26, 2781).

2 : 5-**Toluquinone-2-monoxime**

$$C_6H_3(CH_3)(:NOH)O$$

identical with nitroso-*m*-cresol.

Benzoyl derivative $C_{14}H_{11}O_3N_2$, m.p. 177°; gives a *dichloride* $C_{14}H_{11}O_3N_2Cl_2$, m.p. 149°, and *dibromide* $C_{14}H_{11}O_3N_2Br_2$, m.p. 159° (Bridge and Morgan, Amer. Chem. J. 1898, 20, 775; 1899, 22, 406).

2 : 5-**Toluquinone-5-monoxime,** identical with nitroso-*o*-cresol, m.p. 134°–135°. By adding the theoretical amount of nitrosyl sulphate to 1 part of *o*-cresol in 30 or 40 parts of water (Nölting and Kohn, Ber. 1884, 17, 370). From toluquinone and hydroxylamine (Goldschmidt and Schmied, *ibid.* 2063). Long needles, oxidised by ferricyanide to nitrocresol.

2 : 5-**Toluquinone dioxime** $C_6H_3(CH_3)(:NOH)_2$. By the action of hydroxylamine hydrochloride on either monoxime (Nietzki and Guitermann, Ber. 1888, 21, 432) or on 2 : 5-dinitroso-toluene (Mehne, *ibid.* 733). From 5-nitroso-2-ethyltoluidine (O. Fischer, Annalen, 1895, 286, 163). Explodes on heating.

Diacetyl derivative, m.p. 120°; *benzoyl derivative*, m.p. 135°–136°; and dibromide, m.p. 165° (Bridge and Morgan).

Monochlorotoluquinones and derivatives (Claus and Schweitzer, Ber. 1886, 19, 928; Claus and Jackson, J. pr. Chem. 1888, ii. 38, 328; Schniter, Ber. 1887, 20, 2286; Vorländer and Schrödter, *ibid.* 1901, 34, 1653; Kehrmann and Tichvinsky, Annalen, 1898, 303, 16; Oliveri-Tortorici, Gazz. chim. ital. 1897, 27, ii. 575; Morgan, Amer. Chem. J. 1899, 22, 407; Kehrmann, Ber. 1915, 48, 2021; 1916, 49, 1211).

Dichlorotoluquinones $C_6H(CH_3)\cdot Cl_2O_2$ (Southwarth, Annalen, 1873, 168, 274).

Trichloro-2 : 5-toluquinone $C_6(CH_3)Cl_3O_2$, by chlorination of *o*- and *m*-cresol, and in small quantities from thymol, m.p. 232° or 238° (Borgmann, Annalen, 1869, 152, 248; Southwarth, *ibid.* 1873, 168, 273; Claus and Hirsch, J. pr. Chem. 1889, ii. 39, 59; Claus and Riemann, Ber. 1883, 16, 1602; Hayduck, Annalen, 1874, 172, 209; Knapp and Schultz, *ibid.* 1881, 210, 176; Seelig, *ibid.* 1887, 237, 145; Elbs and Brunschweiler, J. pr. Chem. 1895, ii. 52, 559; Crowther and McCombie, Chem. Soc. Trans. 1913, 103, 536).

Tetrachlorotoluquinone $C_6(CH_2Cl)Cl_3O_2$, m.p. 266°–270° (Gorup, Annalen, 1867, 143, 159; Braeuninger, *ibid.* 1877, 185, 352; Richter, Ber. 1901, 34, 4296).

Bromo-2 : 5-toluquinone $C_6H_2(CH_3)BrO_2$, 3-derivative, m.p. 93°; 4-derivative, m.p. 106° (Claus and Jackson, J. pr. Chem. 1888, ii. 38, 326; Schniter, Ber. 1887, 20, 2286; Gattermann, *ibid.* 1894, 27, 1931; Kehrmann and Rust, Annalen, 1898, 303, 25; Bridge, Amer. Chem. J. 1898, 20, 773; Morgan, *ibid.* 1899, 22, 405). *5-sulphono-derivative* of *3-bromotoluquinone* $C_6H_2(CH_3)Br(:SO_2)O$: a yellow solution is obtained by adding potassium acetate to an acetone solution of bromocresol-sulphonyl chloride. The sulphono-quinone is obtained in a colourless polymeric form (Zincke and Brune, Ber. 1911, 44, 188).

Dibromo-2 : 5-toluquinones $C_6H(CH_3)Br_2O_2$ (Canzoneri and Spica, Gazz. chim. ital. 1882, 12, 473; Claus and Dreher, J. pr. Chem. 1889, ii. 39, 370).

Tribomo-2 : 5-toluquinone $C_6(CH_3)Br_3O_2$, m.p. 235°–236° (Canzoneri and Spica, Gazz. chim. ital. 1882, 12, 470; Auwers and Ziegler, Hampe, v. Erggelet and Burrows, Ber. 1896, 29, 2350; 1899, 32, 3015, 3033, 3040).

Tetrabromo-2 : 5-toluquinone

$$C_6(CH_2Br)Br_3O_2$$

m.p. 258°–259° (Auwers and Hampe, Ber. 1899, 32, 3015).

Pentabromo-2 : 5-toluquinone

$$C_6(CHBr_2)Br_3O_2$$

m.p. 160° (Auwers and Burrows, Ber. 1899, 32, 3038).

Iodo- and **di-iodo-2 : 5-toluquinones** (Kehrmann, J. pr. Chem. 1889, ii. 39, 398, 401).

Chlorobromo-2 : 5-toluquinones

$$C_6H(CH_3)ClBrO_2$$

(Schniter, Ber. 1887, 20, 2287).

Nitro-2 : 5-toluquinone $C_6H_2(CH_3)(NO_2)_2$, m.p. 237° (? *p*-nitrobenzoic acid, Etard, Ann. Chim. 1881, v. 22, 275). *Halogen derivatives* (Zincke, J. pr. Chem. 1901, ii. 63, 186).

3-**Amino-2 : 5-toluquinone**

$$C_6H_2(CH_3)(NH_2)O_2$$

The hydrochloride of the 5-imine is obtained from diaminocresol dihydrochloride at −15°; it is light red in colour. At ordinary temperature the dark red hydrochloride of the 3-imine of 5-amino-2 : 3-toluquinone is obtained (Piccard, Ber. 1909, 42, 4332).

4-**Amino-2 : 5-toluquinone**

$$C_6H_2(CH_3)(NH_2)O_2$$

Several derivatives are known.

Imine $C_6H_2(CH_3)(NH_2)(:NH)O$. Salts are obtained by oxidation of diamino-cresol

$$(CH_3 : OH : NH_2 : NH_2 = 1 : 5 : 2 : 4)$$

(Kehrmann and Prager, Ber. 1906, 39, 3440).

2-p-Tolylimine. From the di-*p*-tolylimine by the action of hydrogen chloride on its alcoholic solution at 25°, pouring into water and precipitating with sodium acetate. Small reddish-brown crystals, m.p. 143°–145° (Green, Ber. 1893, 26, 1775; compare Klinger and Pitschke, *ibid.* 1884, 17, 2442, and Barsilowsky, J. Russ. Phys. Chem. Soc. 1887, 19, 146).

2-Phenyl-5-p-tolyldiimine, m.p. 204° (Green).

Di-p-tolyldiimine

$$C_6H_2(CH_3)(NH_2)(:N\cdot C_7H_7)_2$$

360 grms. of potassium dichromate, 212 grms. of *p*-toluidine and 400 grms. of concentrated sulphuric acid in 40 litres solution in water are allowed to stand 2–3 hours at 5°. The raw product is dissolved in cold glacial acetic acid, diluted with water and saturated with sodium carbonate. The precipitate is then extracted with hot alcohol and crystallised from xylene. This compound has also been obtained by oxidation of *p*-toluidine and of *o*-amino-*m*, *p*-ditolylamine (Barsilowsky, Annalen, 1881, 207, 102; J. Russ. Phys. Chem. Soc. 1887, 19, 141; Perkin, Chem. Soc. Trans. 1880, 37, 546; Klinger and

Pitschke, Ber. 1884, 17, 2440; Green, *ibid.* 1893, 26, 2774; Börnstein, *ibid.* 1901, 34, 1274). Dark red plates, m.p. 235°. Soluble in concentrated sulphuric acid with greenish-blue colour. On warming the solution, *p*-toluidine is split off, the colour changing to Bordeaux red. For other reactions, *see* references given.

Anilino-2 : 5-toluquinone

$C_6H_2(CH_3)(NHC_6H_5)O_2$

Two isomers of m.p. 144°–145° (Hagen and Zincke, Ber. 1883, 16, 1559) and m.p. 148° ($\cdot NHC_6H_5$ in position 4 or 6), Jacobson, Annalen, 1895, 287, 151) are known.

Anilino-2 : 5-toluquinonephenylimine

$C_6H_2(CH_3)(NHC_6H_5)(:NC_6H_5)O$

m.p. 151° (O. Fischer and Hepp, Annalen, 1890, 256, 259).

***o*-Nitroanilino-2 : 5-toluquinone**

$C_6H_2(CH_3)(NHC_6H_4NO_2)O_2$

decomposes at 200° (Leicester, Ber. 1890, 23, 2796). Yields quinonephenotolazine

$$CH_3\cdot C_6HO_2\langle \begin{matrix} N \\ N \end{matrix} \rangle C_6H_4$$

with alcoholic ammonium sulphide at 100°.

Toluidino-2 : 5-toluquinones

$C_6H_2(CH_3)(NHC_7H_7)O_2$

and derivatives (Jacobson, Annalen, 1895, 287, 192, 198; Leicester, Ber. 1890, 23, 2796; Börnstein, *ibid.* 1901, 34, 1274, 4348; compare Perkin, Ber. 1880, 13, 1874).

Diethyl diglycino-2 : 5-toluquinone, m.p. 162°. From ethyl glycine and toluquinone in alcoholic solution (E. Fischer and Schrader, Ber. 1910, 43, 525).

Dianilino-*p*-toluquinone

$C_6H(CH_3)(NHC_6H_5)_2O_2$

From aniline and toluquinone in alcoholic solution, m.p. 232°–233° (Hagen and Zincke, Ber. 1883, 16, 1559). *Phenylimine*, m.p. 167° (Hagen and Zincke) or 172°–173° (O. Fischer and Hepp, Ber. 1888, 21, 678).

Ditoluidinotoluquinones

$C_6H(CH_3)(NHC_7H_7)_2O_2$

and derivatives (O. Fischer and Hepp, *ibid.* 1888, 21, 679; Annalen, 1890, 256, 259: 1891, 262, 251).

3-Hydroxy-2 : 5-toluquinone

$C_6H_2(CH_3)(OH)O_2$

The 2-*oxime* is identical with nitrosoorcinol. Red prisms giving a yellow modification on heating, transition point 128°. Possibly the two modifications are ketonic and enolic forms (Henrich, Monatsh. 1897, 18, 142; Ber. 1897, 29, 989; Zeitsch. physikal. Chem. 1897, 24, 187; Farmer and Hantzsch, Ber. 1899, 32, 3108; Hantzsch and Sluiter, *ibid.* 1906, 39, 162).

4-Hydroxy-2 : 5-toluquinone, m.p. 142°. By oxidation of 2 : 4 : 5-trihydroxytoluene with ferric chloride. *Acetyl- derivative*, m.p. 75°–76° (Thiele and Winter, Annalen, 1800, 311, 350). *Halogen- derivatives* (Spica and Magnanini, Gazz. chim. ital. 1883, 13, 312; Henrich, Taubert and Birkner, Ber. 1912, 45, 303).

Anilinohydroxy-2 : 5-toluquinone decomposes at 250°, its *phenylimine*; *methyl ether*, m.p. 131°; *ethyl ether*, m.p. 115°–116°; and *isobutyl ether*, m.p. 117°, have been prepared (Hagen and Zincke, Ber. 1883, 16, 1560).

Ethoxy-2 : 5-toluquinone is known as the *p-tolylimine*, m.p. 76° (Jacobson and Piepenbrink, Ber. 1894, 27, 2710).

3 : 6-Dihydroxy-2 : 5-toluquinone

$C_6H(CH_3)(OH)_2O_2$

m.p. 177°. From anilinohydroxytoluquinonephenylimine and dilute aqueous potash (Hagen and Zincke, Ber. 1883, 16, 1562).

4-Chloro-3-hydroxy-2 : 5-toluquinone, m.p. 181°–182° (Henrich, Taubert and Birkner, Ber. 1912, 45, 303).

Chlorodihydroxy-2 : 5-toluquinone (Knapp and Schultz, Annalen, 1881, 210, 177; Levy and Bickel, *ibid.* 1889, 249, 69).

Dichlorodihydroxytoluquinone (Braeuninger, Annalen, 1877, 185, 354).

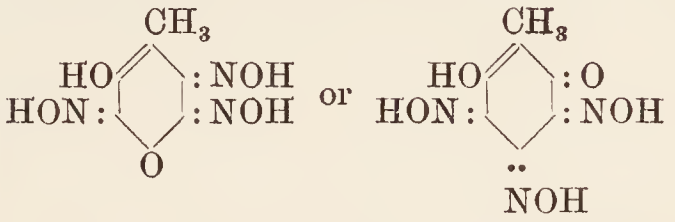
4-Nitro-3 : 6-dihydroxy-2 : 5 : toluquinone (*tolunitranilic acid*), $C_6(CH_3)(NO_2)(OH)_2O_2$. From the potassium salt which is obtained by the action of potassium nitrite on trichlorotoluquinone. Melts and decomposes at 180° (Kehrmann and Brasch, J. pr. Chem. 1889, ii. 39, 378).

Trihydroxy-2 : 5-toluquinone

$C_6(CH_3)(OH)_3O_2$

By action of hydrochloric acid on aminodiiminoorcinol hydrochloride. *Triacetyl- derivative* (Merz and Zetter, Ber. 1879, 12, 2044).

Toluene-diquinone $C_6H(CH_3)O_4$. Known as *tri-* and *tetra-oximes*. The former,



m.p. 189°–190°, is obtained by the action of hydroxylamine hydrochloride on dinitrosomethylphloroglucinol (Weidel and Pollak, Monatsh. 1900, 21, 58).

Ethyl-*p*-benzoquinone $C_6H_3(C_2H_5)O_2$, from ethyl indophenol; m.p. 38·2° (Bayrac, Bull. Soc. chim. 1894, iii. 11, 1130).

2-Ethyl-3 : 5 : 6-tribromo-*p*-benzoquinone, m.p. 118°–120° (Zincke, Ber. 1901, 34, 255).

1 : 2-Dimethyl-4 : 5-benzoquinone

$C_6H_2(CH_3)_2O_2$

By oxidising 5-amino-4-hydroxy-1 : 2-xylene in dilute sulphuric acid with potassium dichromate. Red crystals, m.p. 102°; far more stable than *o*-benzoquinone (Diepolder, Ber. 1909, 42, 2921). *Dichlorodiimine* $C_6H_2(CH_3)_2(:NCl)_2$, explodes at 87° (Noelting and Thesmar, Ber. 1902, 35, 643).

1 : 3-Dimethyl-4 : 5-benzoquinone. The *dioxime* $C_6H_2(CH_3)_2(:NOH)_2$, m.p. 142°, is obtained by reducing dinitrosoxylene with hydroxylamine (Zincke and Schwarz, Annalen, 1899, 307, 48); anhydride, *xylylenefurazane*, m.p. 60°.

2 : 6-Dichloro-1 : 3-dimethyl-4 : 5-benzoquinone, m.p. 108° (Francke, Annalen, 1897, 296, 206).

1 : 2-Dimethyl-3 : 6-benzoquinone (*o-xyloquinone*), m.p. 55° (Noelting and Forel, Ber. 1885, 18, 2673); *dichlorodiimine*, m.p. 105·5° (Noelting and Thesmar, *ibid.* 1902, 35, 649).

4 : 5-Dichloro-1 : 3-dimethyl-4 : 5-benzoquinone, m.p. 159° (Claus and Berkefeld, J. pr. Chem. 1891, ii. 43, 584).

1 : 3-**Dimethyl**-4 : 5-**benzoquinone**, m.p. 72°–73° (Noelting and Baumann and Forel, Ber. 1885, 18, 1151, 2679). *Dichlorodiimine*, m.p. 112° (Noelting and Thesmar); *halogen-, hydroxy- derivatives*, &c. (Fittig and Siepermann, Annalen, 1876, 180, 27; Jacobsen, *ibid.* 1879, 195, 271; Claus and Runschke, J. pr. Chem. 1890, ii. 42, 134; Klages, Ber. 1896, 29, 314; Brunnmayd, Monatsh. 1900, 21, 9; Bose, *ibid.* 1027).

1 : 4-**Dimethyl**-2 : 5-**benzoquinone** (p-*xyloquinone* or *phlorone*), $C_6H_2(CH_3)_2O_2$, has been obtained from the higher homologues of phenol contained in coal-tar (Rommier and Bouilhon, Jahresb. 1862, 322; Carstanjen, J. pr. Chem. 1881, ii. 23, 423), and beech-tar (Rad, Annalen, 1869, 151, 158) by distillation with manganese dioxide and dilute sulphuric acid. Also by oxidising diamino-*p*-xylene (Nietzki, *ibid.* 1882, 215, 168); *p*-xylidine (Carstanjen; Noelting, Witt and Forel, Ber. 1885, 18, 2667); and pseudocumidine (Noelting and Baumann, *ibid.* 1885, 18, 1151). Synthesised by warming butane-dione (diacetyl) with excess of dilute caustic soda solution (v. Pechmann, *ibid.* 1888, 21, 1420), m.p. 125°; triclinic (Muthmann, Jahresb. 1889, 1634). *Dichlorodiimine*, m.p. 137° (Noelting and Thesmar, Ber. 1902, 35, 649). *Indophenol*

$$O{:}C_6H_2(CH_3)_2{:}N{\cdot}C_6H_4{\cdot}N(CH_3)_2$$

m.p. 125°–126° (Bayrac, Bull. Soc. chim. 1894, iii. 11, 1134; Dufet, Ann. Chim. 1897, vii. 10, 58). *Monooxime* $C_6H_2(CH_3)_2(:NOH)O$, identical with nitroso-*p*-xylenol, long red needles, m.p. 165° (Oliveri, Gazz. chim. ital. 1882, 12, 162; H. Goldschmidt and Schmid, Ber. 1885, 18, 568; Salkowski, *ibid.* 1887, 20, 978; Pflug, Annalen, 1889, 255, 174). *Dioxime*, m.p. 254° (Sutkowski, Ber. 1887, 20, 978; Pflug); *diacetyl-derivative*, m.p. 170°.

Halogen derivatives of phlorone; *see* Carstanjen, Rad, Auwers and Baum (Ber. 1896, 29, 2341); Auwers and Sheldon (Annalen, 1898, 301, 276); Auwers and Rapp (*ibid.* 1898, 302, 165); Auwers and Sigel (Ber. 1902, 35, 436); Teichner (*ibid.* 2303).

Dihydroxy-*p*-xyloquinone $C_6(CH_3)_2(OH)_2O_2$. By condensation of ethyl oxalate and propionate with sodium; m.p. 245°. *Di-acetyl-derivative*, m.p. 146·5° (Fichter and Willmann, Ber. 1904, 37, 2384; Annalen, 1908, 361, 363).

Dianilino-*p*-xyloquinone, m.p. 264° (Pflug, Annalen, 1889, 255, 171).

1 : 2 : 4-**Trimethyl**-5 : 6-**benzoquinone.** The *monochloro- derivative* $C_6Cl(CH_3)_3O_2$ obtained from trimethylchlorocatechol, m.p. 96°–97° (Hodes, Annalen, 1897, 296, 218).

1-**Propyl**-2 : 5-**benzoquinone.** *Methoxy-derivative* $C_6H_2(OCH_3)(C_3H_7)O_2$, m.p. 111°, by reducing an alcoholic solution of asarone with sodium (Ciamician and Silber, Ber. 1890, 23, 2294).

1-**Isopropyl**-2 : 5-**benzoquinone**

$$C_6H_3[CH(CH_5)_2]O_2$$

m.p. 28·4° (Bayrac, Bull. Soc. chim. 1895, iii. 13, 984). Derivatives (Hoffmann, Ber. 1901, 34, 1559; Böters, *ibid.* 1902, 35, 1505).

1-**Methyl**-4-**ethyl**-2 : 5-**benzoquinone**

$$C_6H_2(CH_3)(C_2H_5)O_2$$

m.p. 55·3°, and *dimethylaminophenylimine*, m.p. 77° (Bayrac, Bull. Soc. chim. 1895, iii. 13, 897).

1 : 2 : 4-**Trimethyl**-3 : 6-**benzoquinone** (*cumoquinone*), m.p. 11° (Noelting and Baumann, Ber. 1888, 18, 1152; Nietzki and Schneider, Ber. 1894, 27, 1430). *Oxime*, m.p. 184°; 5-*chloro-derivative*, m.p. 72°–73°; 5-*nitro- derivative*, m.p. 113° (Nef, Annalen, 1887, 237, 17).

1-**Methyl**-4-**propyl**-2 : 5-**benzoquinone**

$$C_6H_2(CH_3)(C_3H_7)O_2$$

m.p. 18° (Bayrac, Bull. Soc. chim. 1895, iii. 13, 979). *Dibromo- derivative*, m.p. 30° (Claus and Herfeldt, J. pr. Chem. 1891, ii. 43, 579).

1-**Methyl**-2-**isopropyl**-3 : 6-**benzoquinone**

$$C_6H_2[CH_3][CH(CH_3)_2]O_2$$

m.p. 40° (Claus and Raps, J. pr. Chem. 1891, ii. 43, 576).

1-**Methyl**-3-**isopropyl**-2 : 5-**benzoquinone**, m.p. 32° (Claus and Herfeldt, *l.c.*).

Thymoquinone $C_6H_2(CH_3)(i\text{-}C_3H_7)O_2$, m.p. 45·5°, has been found in the oil of wild bergamot, *Monardia fistulosa* (Brandel and Kremers, Pharm. Review, 1901, 19, 200, 244). Obtained from thymol (Lallemand, Jahresb. 1854, 592); cymophenol $C_6H_3(CH_3)(C_3H_7)(OH)$ (Carstanjen, J. pr. Chem. 1877, ii. 15, 410) and dithymolethane $CH_3{\cdot}CH(C_{10}H_{12}OH)_2$ (Steiner, Ber. 1878 11, 289) by distillation with manganese dioxide and dilute sulphuric acid, or by the oxidation of aminothymol (Andresen, J. pr. Chem. 1881, ii. 23, 172; Armstrong, Ber. 1877, 10, 297; Liebermann and Ilinski, *ibid.* 1885, 18, 3194). By the hydrolysis of the indophenol from dimethyl-*p*-phenylenediamine and thymol (Bayrac, Bull. Soc. chim. 1892, iii. 7, 99); by oxidation of carvacrol with chromic acid mixture (Reychler, Bull. Soc. chim. 1892, iii. 7, 32); and by oxidation of thymohydroquinone with benzoquinone (Biltris, Bull. Acad. roy. Belge, 1898, iii. 35, 44; Valeur, Ann. Chim. 1900, vii. 21, 553); m.p. 45·5°; b.p. 232°; heat of combustion 1274·6 cal. (Valeur, Compt. rend. 1897, 125, 872). For other properties and reactions, *see* Liebermann (Ber. 1885, 18, 3196), Ciamician and Silber (Real. Accad. d. Linc. 1901, v. 10, i. 96), Jackson and Oenslager (Amer. Chem. J. 1896, 18, 20), Biltris (*l.c.*), Valeur (*l.c.*).

Thymoquinone gives *bithymoquinone*, a polymer of m.p. 200°–201°, when its ethereal solution is exposed to light; it is largely reconverted into thymoquinone on distillation (Liebermann and Ilinski, Ber. 1885, 18, 3195), and gives an oxime, m.p. 264, and dioxime, m.p. 290°, differing from those of thymoquinone.

Two *thymoquinonedimethylaminophenylimines* $O{:}C_6H_2(CH_3)(C_3H_7){:}N{\cdot}C_6H_4{\cdot}N(CH_3)_2$ are known, (i.) from thymol and dimethyl-*p*-phenylenediamine (N=5), melts at 69·5°; (ii.) from carvacrol (N=2) at 87°–88° (Bayrac, Bull. Soc. chim. 1892, iii. 7, 97; 1894, iii. 11, 1135; Dufet, Zeitsch. Kryst. 1897, 27, 631).

Thymoquinone-chloroimine

$$C_6H_2(CH_3)(C_3H_7)(O)(HCl)$$

explodes at 160°–170° (Andersen, J. pr. Chem. 1881, ii. 23, 169).

Thymoquinone-2-oxime

$$C_6H_2(CH_3)(C_3H_7)(O)(:NOH)$$

identical with nitrosothymol, m.p. 160°–162° (R. Schiff, Ber. 1875, 8, 1500; Goldschmidt and Schmied, *ibid.* 1884. 17, 2061; Liebermann and

Ilinski, *ibid.* 1885, 18, 2194; Widmann, *ibid.* 1882, 15, 171; Liebermann, *ibid.* 1877, 10, 78; Sutkowski, *ibid.* 1886, 19, 2315; Plancher, Gazz. chim. ital. 1895, 25, ii. 385; Oliveri-Tortorici, *ibid.* 1897, 27, ii. 580; Valeur, Bull. Soc. chim. 1898, iii. 19, 516; Klages, Ber. 1899, 32, 1518).

Thymoquinone-5-oxime, identical with nitroso-carvacrol, m.p. 153° (Mazzara and Plancher, Gazz. chim. ital. 1891, 21, ii. 155; Paternò and Canzoneri, Ber. 1879, 12, 383; Plancher, Gazz. chim. ital. 1895, 25, ii. 391; Klages, Ber. 1899, 32, 1518). 3-*Chloro- derivative*, m.p. 157°–158° (Oliveri-Tortorici, Gazz. chim. ital. 1897, 27, ii. 582; Kehrmann, Krüger and Schön, Annalen, 1900, 310, 95, 108; Stroesco, Zeitsch. Kryst. 1899, 30, 75).

Thymoquinone-dioxime

$$C_6H_2(CH_3)(C_3H_7)(:NOH)_2$$

has been obtained from nitrosothymol (Kehrmann and Messinger, Ber. 1890, 23, 3558) or nitrosocarvacrol and hydroxylamine (Oliveri-Tortorici, Gazz. chim. ital. 1900, 30, i. 534). Does not melt; decomposes at 255° (Kehrmann and Messinger) or at 235° (Oliveri-Tortorici). *Acetyl- derivative* (Böhm, Ber. 1895, 28, 1547); and *diacetyl- derivative*, two modifications, each melting at 110°.

Numerous *halogen*, *alkylamino-*, anilino-, &c., derivatives of thymoquinone have been prepared; for literature, *see* Andresen (J. pr. Chem. 1881, ii. 23, 178); Schniter (Ber. 1887, 20, 1317); Carstanjen (J. pr. Chem. 1871, ii. 3, 55); Mazzara and Discalzo (Gazz. chim. ital. 1886, 16, 197); Kehrmann (Ber. 1889, 22, 3264; J. pr. Chem. 1889, ii. 39, 394; 1889, ii. 40, 188); Zincke (Ber. 1881, 14, 94); H. Schulz (*ibid.* 1883, 16, 900); Anschütz and Leather (Annalen, 1887, 237, 115); Ladenburg (Ber. 1877, 10, 49, 1220); Liebermann (*ibid.* 1877, 10, 79, 613); Mazzara (*ibid.* 1890, 23, 1392); Kowalski (*ibid.* 1892, 25, 1661); Kehrmann and Krüger (Annalen, 1900, 310, 89); Stroesco (Zeitsch. Kryst. 1899, 30, 75); Hoffmann (Ber. 1901, 34, 1558); Böters (*ibid.* 1902, 35, 1505); Wakeman and Groffman (Science, 1921, 53, 218).

Dihydroxythymoquinone, m.p. 220°–221°. *Diacetate*, m.p. 81°; *dibenzoate*, m.p. 163°. Reduction products (Wakeman, J. Amer. Chem. Soc. 1919, 41, 1873).

1 : 4-**Diethyl - 3 : 6 - dihydroxy - 2 : 5 - benzoquinone**, m.p. 217°–218°. *Diacetate*, m.p. 130°; *dibenzoate*, m.p. 201° (Fichter, Annalen, 1908, 361, 363).

Tetramethyl-*p*-benzoquinone or **duroquinone** $C_6(CH_3)_4O_2$ is obtained by the oxidation of diaminodurene with ferric chloride (Nef, Annalen, 1887, 237, 5). For a convenient method of preparation, starting with pseudo-cumene and converting this by the Friedel-Crafts reaction into durene, *see* Rügheimer and Hankel (Ber. 1896, 29, 2172). Also obtained from pentane-2 : 3-dione (von Pechmann, *ibid.* 1888, 21, 1420) and 3, 3-dichloropentane-2-one (Faworsky, J. pr. Chem. 1895, ii. 51, 538), m.p. 111°. Yields *biduroquinone*,

$$\begin{array}{l} CH_3\cdot C\cdot CO\cdot C\cdot CH_2\cdot C(OH)\cdot C(CH_3) : C\cdot CH_3 \\ \quad\quad\| \quad\quad\| \quad\quad\quad\

and Soch, Ber. 1900, 33, 1241). The *monoxime* and its benzoyl derivative have been prepared, whilst 4-*anilino*-1 : 3-diphenylbenzo-2 : 5-quinone m.p. 167°, is formed when the quinone is boiled with aniline.

1 : 4-**Diphenyl-2 : 5-benzoquinone**

$C_6H_2(C_6H_5)_2O_2$

m.p. 214°. By alkaline condensation of methylphenyldiketone. Orange yellow leaflets (Müller and von Pechmann, Ber. 1889, 22, 2131). Diphenyldihydroxy-*p*-benzoquinone and Dibenzyldihydroxy-*p*-benzoquinone (Fichter, Annalen, 1908, 361, 363).

1 : 4-**Dibenzhydryl-2 : 5-benzoquinone**

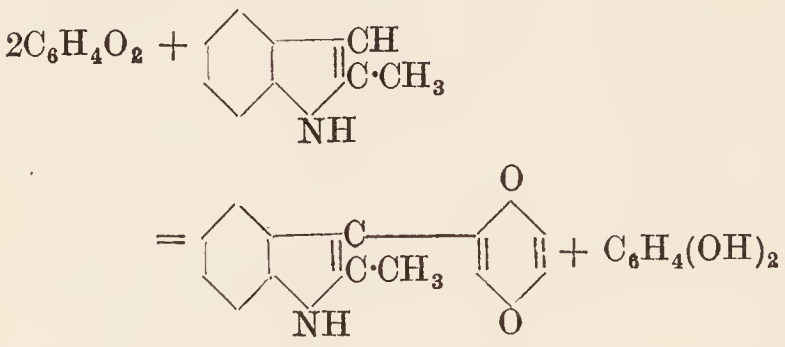
$C_6H_2[CH(C_6H_5)_2]_2O_2$

By condensation of benzoquinone with benzhydrol, m.p. 250° (indef.) (Möhlau, Ber. 1898, 31, 2351 ; Möhlau and Klopfer, *ibid.* 1899, 32, 2147). The *octamethyltetraamino- derivative*

$C_6H_2[CH\{C_6H_4\cdot N(CH_3)_2\}_2]_2$

is obtained by warming benzoquinone with Michler's hydrol for 6 hours in alcoholic solution ; m.p. 245°.

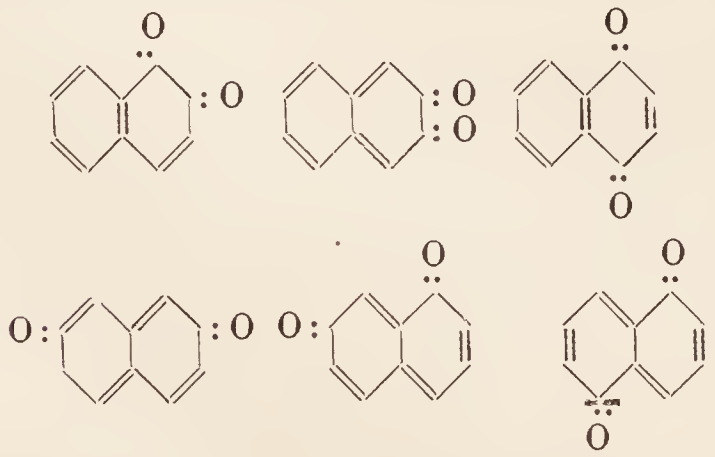
Other substituted benzoquinones are obtained by the action of substances of the indole series on quinone. Thus α-methylindole reacts as follows :



e.g. *α-methylindyl*-p-*benzoquinone*, m.p. 185°. *N-methyl - α - methylindyl - p - benzoquinone*, m.p 160° ; *α-phenylindyl*-p-*benzoquinone*, m.p. 205°, and other substances. Tetrahydroquinoline also reacts, giving $C_6H_2(C_9H_{10}N)_2O_2$, m.p. 189° (Möhlau and Redlich, Ber. 1911, 44, 3605).

Quinones $C_nH_{2n-14}O_2$.

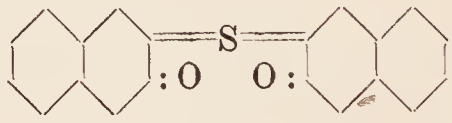
Naphthaquinones. Six naphthaquinones are possible.



The 1 : 2-, 1 : 4-, and 2 : 6-quinones have been prepared. The first two have been known for a long period, the 2 : 6-quinone was obtained by Willstätter and Parnas (Ber. 1907, 40, 1406, 3971). 2 : 3-Naphthaquinone is represented by the 4-chloro-6-bromo-1-methyl derivative (Fries and Empson, Ber. 1909, 42, 3375).

Dinaphthadiquinones. The following are known, viz. 1 : 1′-dinaphtha-3 : 4 : 3′ : 4′-diquinone (Stehhouse and Groves, Annalen, 1878, 194, 205; Chem. Soc. Trans. 1878, 33, 415; Zincke and Rathgen, Ber. 1886, 19, 2483); 2 : 2′-dinaphtha-1 : 4 : 1′ : 4′-diquinone (Staub and Smith, Chem. Soc. Trans. 1885, 47, 104; Chattaway, *ibid.* 1895, 67, 657; Witt and Dedichen, Ber. 1897, 30, 2663); and a diaphtha-1 : 7 : 1′ : 7′-diquinone in which the position at which the nuclei are joined is undetermined (Morgan and Vining, Chem. Soc. Trans. 1921, 119, 1707).

A peculiar type of quinone containing quadrivalent sulphur and closely related to 1 : 2-naphthaquinone is known. Onufrowicz (Ber. 1890, 23, 3358) obtained a stable scarlet substance, m.p. 155° (158° Smiles) by oxidising the α-sulphide of β-naphthol, this was examined at greater length by Henriques (Ber. 1894, 27, 2999), who considered it to be a peroxide. Hilditch and Smiles (Chem. Soc. Trans. 1911, 99, 977) recognised that the substance was a naphtha-sulphonium quinone with the constitution



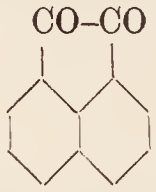
See Smiles and co-workers (Chem. Soc. Trans. 1912, 101, 1420 ; 1913, 103, 350, 901 ; 1914, 105, 1396, 1739, 1746). See article on Naphthalene.

Quinones $C_nH_{2n-16}O_2$.

Phenylquinone $C_6H_3(C_6H_5)O_2$ is dealt with earlier in this article.

Quinones $C_nH_{2n-18}O_2$.

Acenaphthenequinone $C_{12}H_6O_2$, or



m.p. 262°–263°.

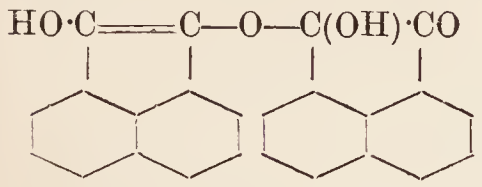
This compound is not strictly a quinone, the two carbonyl groups being situated in a 5-membered ring. It has been prepared by oxidation of acenaphthene $C_{12}H_{10}$ with chromic acid mixture, &c. ; the yields are not, however, good (Graebe, Ber. 1887, 20, 659 ; Graebe and Gfeller, *ibid.* 1892, 25, 654 ; Annalen, 1893, 276, 1). Better results have been obtained by hydrolysing the monooxime obtained by the action of alkyl nitrites on acenaphthene.

When four molecular proportions of amyl nitrite are added to a boiling solution of acenaphthene whilst a stream of hydrogen chloride is passed in, two isomeric acenaphthenequinoneoximes $C_{12}H_6(:NOH)O$ are produced. These may be separated by difference of acidity, one being insoluble in hot sodium carbonate solution. When this is rapidly crystallised from glacial acetic acid, small pale yellow crystals which decompose at 207° are obtained. If the boiling with acetic acid be continued some time, water precipitates the oxime of m.p. 230°, which can be obtained from acenaphthenequinone and hydroxylamine (Francesconi and Pirazzoli, Gazz. chim. ital. 1903, 33, i. 42).

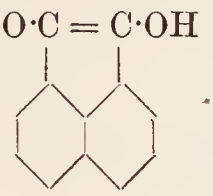
To prepare acenaphthene quinone, the oxime of higher m.p. is dissolved in 7 times its weight of 75 p.c. sulphuric acid and heated for 1 hour

on the water-bath. Water is added, the quinone filtered off, digested for some time with warm dilute caustic soda and recrystallised from glacial acetic acid (Kalle and Co., D. R. P. 228698, 1909; Reissert, Ber. 1911, 44, 1749). For the oxine, m.p. 220° is given.

Acenaphthene quinone yields a compound $C_{12}H_6(C_6H_5)_2O$ (diphenylacenaphthenone) with benzene and aluminium chloride (Zsuffa, Ber. 1910, 43, 2915); on reduction compounds of m.p. 248° and 254° are produced (Kalle and Co., D. R. P. 224979, 1909) to which the constitutions



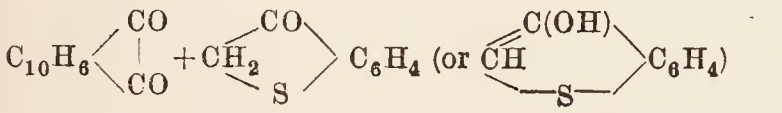
and

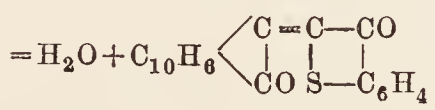


have been assigned.

Acenaphthenequinone condenses with substances containing a reactive methylene group. Vat dyestuffs may be produced in this way.

Ciba-scarlet G or *Thioindigo scarlet G* is obtained by condensation with 3-hydroxy (1) thionaphthene



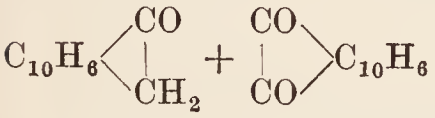


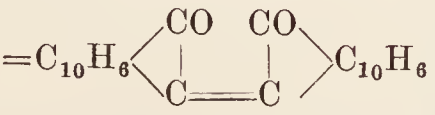
or by heating to 230°–250° with phenylthiolglycol-*o*-carboxylic acid (Basler Chemische Fabrik, D. R. P. 205377, 1907; compare Bezdzik and Friedländer, Monatsh. 1908, 29, 375; A. Grob, Ber. 1908, 41, 331). The acenaphthene quinone may be replaced by dichloroacenaphthenone. The following patents refer to similar condensations (Basler Chemische Fabrik, D. R. PP. 196349, 1907; 198510, 1907; Ges. chem. Ind. Basel, D. R. PP. 210905, 1907; 211696, 1907; 212870, 1908; 213504, 1908).

Ciba scarlet is a yellowish-red powder, sublimes on heating, gives a green solution in concentrated sulphuric acid and is precipitated as red flocks by addition of water. It is used as a vat dyestuff (sodium hyposulphite or sodium sulphide) and in cotton printing.

Ciba red R paste (D. R. P. 213504) is a brominated ciba-scarlet G; its reactions are similar (Grandmougin, Elsässischer Textil-Blatt, 1911).

By the condensation of acenaphthenequinone with acenaphthenone, an orange-red dyestuff, probably identical with the 'biacenaphythylidenedione' of Graebe and Gfeller (Annalen, 1893, 276, 17) and Graebe and Jequier (*ibid.* 1896, 290, 199), is obtained





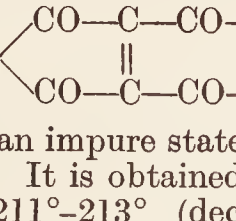
The condensation can be effected in absolute alcoholic solution with sodium carbonate or sodium acetate and acetic anhydride may be used (Ges. chem. Ind. Basel, D. R. P. 212858, 1908).

18 parts of acenaphthenequinone, 16·5 parts of acenaphthenone and 3 parts of fused sodium acetate are heated with 100 parts of acetic anhydride to boiling under reflux. The product separates as orange-needles which are collected after cooling, washed and dried.

Acenaphthenone itself may be conveniently prepared by treating α-naphthylacetyl chloride in nitrobenzene with aluminium chloride dissolved in the same solvent (Badische Anilin- und Soda-Fabrik, D. R. P. 230237, 1909).

For other derivatives of acenaphthene, quinone, *see* F. Mayer and W. Kaufmann (Ber. 1920, 53, 289), Fleischer and Wolff (*ibid.* 925), Rowe and Davies (Chem. Soc. Trans. 1920, 117, 1344). These authors have prepared the *dioxime* of 2 : 3-acenaphthenequinone, O. Gerhardt (Monatsh. 1921, 42, 63), A. Schönberg (Ber. 1921, 54, 2838).

A diketone of similar type to acenaphthenequinone is aceanthrenequinone



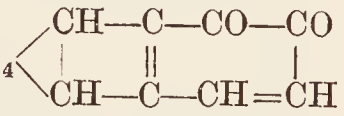
red prisms, m.p. 270°, obtained from anthracene and oxalyl chloride (Liebermann and Zsuffa, Ber., 1911, 44, 208).

For reactions and derivatives, *see* Liebermann and Butescu (Ber. 1912, 45, 1213), Butescu (Ber. 1913, 46, 212), Liebermann and Kardos (Ber. 1914, 47, 1203).

Quinones $C_nH_{2n-20}O_2$.

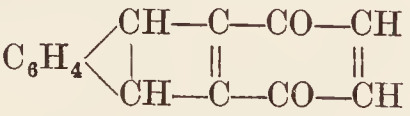
Anthraquinone $C_{14}H_8O_2$ and its derivatives are described in a special article (*q.v.*).

The following compounds give the specific reactions of quinones, which are usually wanting in the case of ordinary (9 : 10) anthraquinone.

1 : 2-**Anthraquinone** 

m.p. about 180° (with decomposition), has been obtained by the oxidation of 1-amino-2-hydroxyanthracene (Lagodzinski, Ber. 1894, 27, 1438; 1895, 28, 1422).

1 : 4-**Anthraquinone**



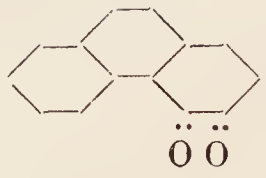
long yellow needles, m.p. 206°, is obtained from 4-nitroso-1-anthrol by reduction with stannous chloride, followed by oxidation with ferric chloride (Dienel, Ber. 1906, 39, 926).

1 : 4 : 9 : 10-**Anthradiquinone**

was obtained in an impure state by Lesser (Ber. 1914, 47, 2526). It is obtained as straw yellow needles, m.p. 211°–213° (decomposition), by the oxidation of a finely divided suspension of quinizarine in glacial acetic acid with lead peroxide (Dimroth and Schultze, Annden, 1916, 411, 345). The glacial acetic acid solution when treated with hydrogen chloride gas gives 3 chloroquinizarine, m.p. 239°–240°.

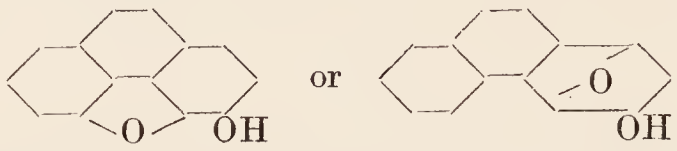
Phenanthraquinone and its derivatives are described in a special article (*v.* PHENANTHRENE).

3 : 4-**Phenanthraquinone**



has been obtained by Barger (Chem. Soc. Trans. 1918, 113, 218), by oxidising an ethereal solution of morphol (3 : 4-dihydroxyphenanthrene), with silver oxide. It forms brilliant red, short, pointed prisms, which blacken at 125°–130°, heated rapidly it melts about 132°–133°. It is reduced immediately to morphol by sulphurous acid.

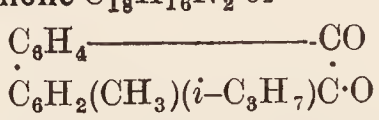
Morphenolquinone $C_{14}H_6O_4$, corresponds to morphenol $C_{14}H_7(OH)O$, which may be written constitutionally as



Vongerichten (Ber. 1900, 33, 352); Schryver and Lees (Chem. Soc. Trans. 1901, 79, 568).

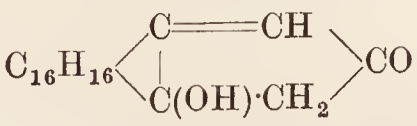
Morphenol is obtained by the action of alcoholic potash on methylmorphimethine, acetylmorphenol when oxidised yields a quinone which furnishes morphenolquinone on hydrolysis. Orange aggregates from glacial acetic acid.

Retenequinone $C_{18}H_{16}N_2$ or

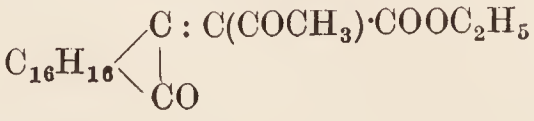


by oxidation of retene with chromic acid (Wahlforss, Zeitsch. Chem. 1869, 73), preferably in acetic acid solution (Bamberger and Hooker, Annalen, 1885, 229, 117). Orange needles, m.p. 197°–197·5°. Very easily soluble in boiling carbon disulphide; for solubility in alcohol, *see* Ekstrand (*ibid.* 1877, 188, 75). Molecular heat of combustion at constant pressure, 2158·0 cal. (Valeur, Bull. Soc. chim. 1898, [iii.] 19, 514). *Perchlorate* $(C_{18}H_{16}O_2)_2{\cdot}HClO_4$ (Hofmann, Metzler and Lecher, Ber. 1910, 43, 182). Yields retene-ketone (1-methyl-4-methoethylfluorenone) on heating with barium hydroxide (Ekstrand, *ibid.* 1884, 17, 692). Shows the usual reactions of an *o*-quinone (azine formation, &c.); with arylhydrazine-sulphonic acids orange-red to blue-red dyestuffs are produced (A.-G. Chem. Ind. Rheinau; D. R. P. 46746, 188). *Imine*, m.p. 109°–111° (Bamberger and Hooker); *oxime*, m.p. 128·5° (B. and H.).

Retenequinone condenses with ketones, thus with acetone it gives anhydracetoneretenequinone,



(Heiduschka and Chudadad, Arch. Pharm. 1913, 251, 401), and with ethyl acetoacetate, a compound of the constitution



(*ibid.* p. 682).

Monobromoretene-quinone $C_{18}H_{15}O_9Br$, m.p. 210°–212° (Wahlforss). *Dibromoretene-quinone* $C_{18}H_{14}Br_2$, m.p. 250°–252° (Bamberger and Hooker).

Diethylreteneindandione gives a quinone $C_{25}H_{24}O_4$, m.p. 193°–194°, on oxidation (Freund and Fleischer, Annalen, 1910, 373, 291).

QUINONES $C_nH_{2n-22}O_2$.

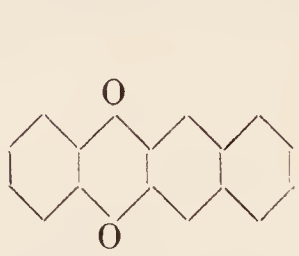
Fluoranthenequinone $C_{15}H_8O_2$, m.p. 188°, by oxidation of fluoranthene with chromic acid mixture: small red needles (Goldschmiedt, Ber. 1877, 10, 2029; Fittig, Gebhard, Liepmann, Annalen, 1878, 193, 149; 1880, 200, 3).

QUINONES $C_nH_{2n-24}O_2$.

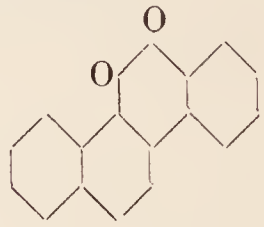
Diphenylbenzoquinone $C_6H_2(C_6H_5)_2O_2$. Has been described previously.

QUINONES $C_nH_{2n-26}O_2$.

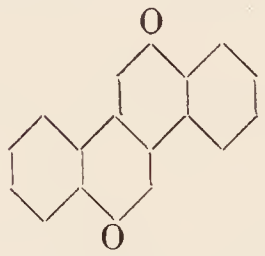
Many quinones $C_{18}H_{10}O_2$ are possible and the following have been obtained.



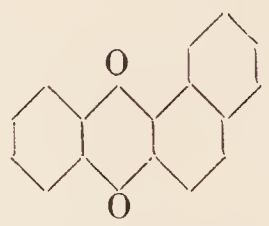
Naphthacenequinone.



1 : 2-Chrysoquinone.

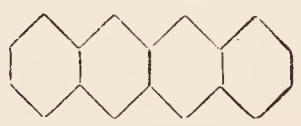


2 : 8-Chrysoquinone.

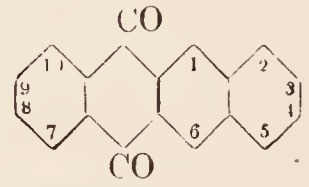


Benzanthraquinone.

Naphthacenequinone $C_{18}H_{10}O_2$, is a paraquinone showing considerable analogy to anthraquinone: it is derived from a parent hydrocarbon naphthacene $C_{18}H_{12}$. The constitutional formulæ of these two compounds and the method of numbering the positions in the naphthacenequinone molecule are shown below.

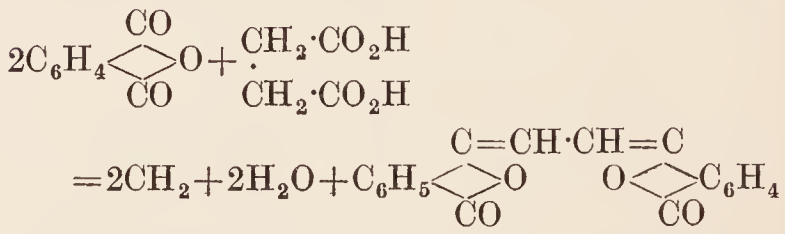


Naphthacene.



Naphthacenequinone.

Gabriel and Michael melted a mixture of phthalic anhydride, succinic acid and fused sodium acetate and obtained ethylene (di)phthalide (Ber. 1877, 10, 1558).

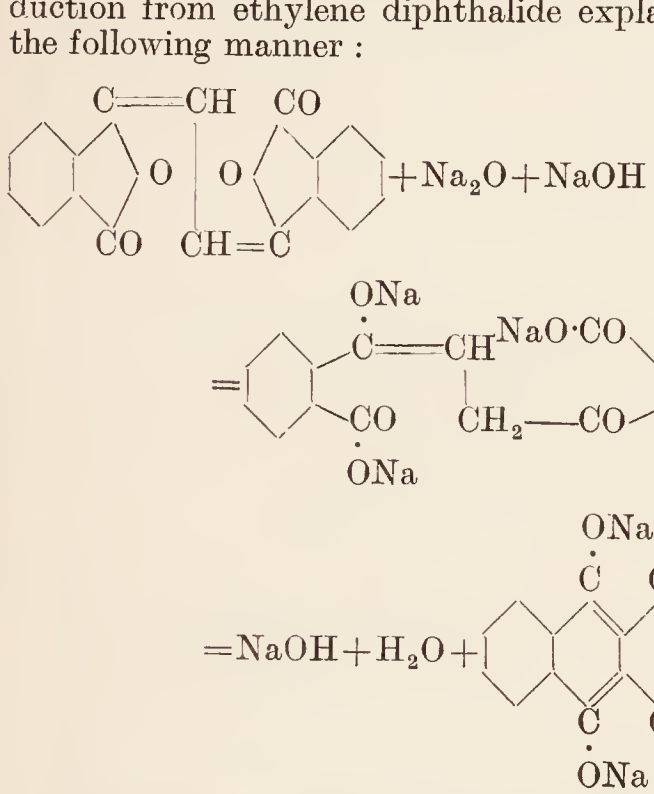


Roser examined the reaction and found that an *iso*-ethylene diphthalide was formed at the same time in small quantity (Ber. 1884, 17, 2774). Gabriel and Leupold improved the method for obtaining the ethylene phthalide (*ibid.* 1898, 31, 1161) and also examined the

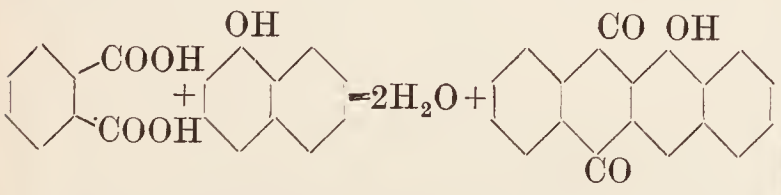
action of sodium methoxide on ethylene diphthalide which had been previously studied by F. Nathanson (*ibid.* 1893, 26, 2582). Nathanson suspended ethylene phthalide in methyl alcohol, added sodium methoxide, evaporated off the methyl alcohol, added hot water, separated from undissolved matter and precipitated the filtrate with hydrochloric acid. The substance so obtained gave results on analysis agreeing with the expected *bis*-diketohydrindene,



Gabriel and Leupold recognised that Roser's *iso*ethylene diphthalide was also formed in the reaction (Ber. 1898, 31, 1272) and found that it contained two hydroxyl groups. On distillation with zinc-dust, hydrocarbons $C_{18}H_{12}$ and $C_{18}H_{14}$ were obtained. The latter evidently contains two CH_2-groups, since on oxidation with chromic acid, a quinone $C_{18}H_{10}O_2$ is produced. This quinone when fused with potash gives benzoic and β-naphthoic acids (anthraquinone when fused with potash gives two molecules of benzoic acid (Graebe and Liebermann, Annalen, 1871, 160, 129), which points to the formula given above for naphthacenequinone. The '*iso*ethylenediphthalide' was found to contain two hydroxyl groups. It can be formulated as a dihydroxynaphthacene quinone, and its production from ethylene diphthalide explained in the following manner :



Another method for the production of naphthacenequinone derivatives was introduced by Deichler and Weizmann (Ber. 1903, 36, 547) who condensed α-naphthol with phthalic acid in presence of concentrated sulphuric acid



Naphthacenequinone $C_{18}H_{10}O_2$. By oxidising 6 grms. of dihydronaphthacene in 360 c.c. of glacial acetic acid with 9 grms. of chromic acid dissolved in 9 c.c. of water and 90 c.c. of glacial acetic acid. Long yellow needles, m.p. 294° (Gabriel and Leupold, Ber, 1898, 31, 1277).

1 - **Chloronaphthacenequinone** $C_{18}H_9ClO_2$. From hydroxynaphthacene quinone and phosphorus pentachloride, m.p. 254° (Orchardson and Weizmann, Chem. Soc. Trans. 1906, 89, 118).

1 : 6-**Dichloronaphthacenequinone**

$C_{18}H_8Cl_2O_2$

From dihydroxynaphthacene quinone and phosphorus pentachloride, m.p. 259°–260° (Gabriel and Leupold, Ber. 1898, 31, 1282).

Bromo-1-chloronaphthacenequinone

$C_{18}H_8ClBrO_2$

m.p. 180° (Orchardson and Weizmann, Chem. Soc. Trans. 1906, 119).

Nitronaphthacenequinone $C_{18}H_9(NO_2)O_2$. By nitration of naphthacene quinone, m.p. 315° (Gabriel and Leupold, *l.c.* 1278).

Dinitronaphthacenequinone $C_{18}H_8(NO_2)_2O_2$. From dihydronaphthacene and nitric acid, m.p. 240° (*ibid.*).

1-**Hydroxynaphthacenequinone**

$C_{18}H_9(OH)O_2$

Prepared by intimately mixing 50 grms. of phthalic acid, 44 grms. of α-naphthol and 50 grms. of boric acid, then adding 500 c.c. of 97 p.c. sulphuric acid and heating to 160°, maintaining the temperature for about 1 hour at 160°–165° until no further alteration in the red coloration is observed. The mixture is poured into water, the precipitate collected and dissolved in a boiling 10 p.c. solution of caustic potash and the potassium salt, which separates on cooling, dissolved in boiling water and decomposed by hydrochloric acid. Long reddish-yellow needles from nitrobenzene, m.p. 303°.

Acetyl derivative $C_{18}H_9(OCOCH_3)O_2$ (Deichler and Weizmann, Ber. 1903, 36, 550).

6-**Chloro-1-hydroxynaphthacenequinone**

$C_{18}H_8Cl(OH)O_2$

m.p. 290°–293°. *Acetyl derivative*, m.p. 270°–273° (Bentley, Friedl, Thomas and Weizmann, Chem. Soc. Trans. 1907, 91, 418).

7 : 10-**Dichloro-1-hydroxynaphthacenequinone** $C_{18}H_7Cl_2(OH)O_2$ (Harrop and Weizmann, *ibid.* 1909, 95, 283).

7:8:9:10-**Tetrachloro-1-hydroxynaphthacenequinone** $C_{18}H_5Cl_4(OH)O_2$ (Harrop and Weizmann, *ibid.* 1909, 95, 287).

Bromo-1-hydroxynaphthacenequinone

$C_{18}H_8Br(OH)O_2$

By brominating 1-hydroxynaphthoylbenzoic acid and condensing with sulphuric acid. With phosphorus pentachloride gives chlorobromonaphthacenequinone of m.p. 180° (Orchardson and Weizmann, Chem. Soc. Trans. 1906, 89, 119).

6-**Nitro-1-hydroxynaphthacenequinone**

$C_{18}H_8(NO_2)(HO)O_2$

By nitration of hydroxynaphthacene quinone, m.p. 274° (Deichler and Weizmann, Ber. 1903, 36, 2326).

Dinitro-1-hydroxynaphthacenequinone

$C_{18}H_7(NO_2)_2(OH)O_2$

m.p. 260° (D. and W. *ibid.* 2327).

2 : 6 ?-**Dinitro-1-hydroxynaphthacenequinone** m.p. 275°. *Acetyl derivative*, m.p. 276°–278°

(Bentley, Friedl, Thomas and Weizmann, Chem. Soc. Trans. 1907, 91, 419).

1 : 5-**Dihydroxynaphthacenequinone**

$C_{18}H_8(OH)_2O_2$

From 1′ : 5′-dihydroxy-2-β-naphthoylbenzoic acid. Brick-red powder, sublimes below 300° (Bentley, Friedl and Weizmann, *ibid.* 1907, 91, 1593).

1 : **Hydroxy**-5 : **methoxynaphthacenequinone** (Bentley, Friedl, Thomas and Weizmann, *ibid.* 1907, 91, 435).

7 : 10-**Dichloro**-1 : 5-**dihydroxynaphthacenequinone** $C_{18}H_6Cl_2(OH)_2O_2$ (Harrop and Weizmann, *ibid.* 1909, 95, 284).

1 : 6-**Dihydroxynaphthacenequinone**

$C_{18}H_8(OH)_2O_2$

75 grms. of crude ethylene phthalide are suspended in 250 c.c. of methyl alcohol, warmed on a water-bath at 60°, and mixed with a solution of 17 grms. of sodium in 300 c.c. of methyl alcohol. The mixture is boiled 20 or 30 minutes under reflux, filtered, and the residue washed with absolute alcohol. By boiling the black residue with 1 litre of water and filtering, a solution of the sodium salt of *bis*-diketohydrindene is obtained (yield of *bis*-diketohydrindene, 32·5 grms., m.p. 297°). The residue of *iso*-ethylenediphthalide and its sodium salt is repeatedly boiled with water and then with dilute hydrochloric acid. Yield 16·5 grms., m.p. 346°–347° (uncorr.) (Gabriel and Leupold, Ber. 1898, 31, 1161).

Liebermann and Flatau (*ibid.* 1901, 34, 2151) found that the potassium salt was formed when *tris*-diketohydrindene was boiled with a solution of two molecules of alkali. They give no melting-point.

Deichler and Weizmann (Ber. 1903, 36, 721) obtained the substance by heating 10 grms of 1-hydroxynaphthacenequinone with 10 grms. of boric acid and 100 grms. of 96 p.c. sulphuric acid 3–4 hours at 230° ; m.p. 300° (uncorr.).

Gabriel and Leupold consider the compound to be identical with the ' indenigo ' obtained by the oxidation of diphthalylethane with hydrogen peroxide or potassium persulphate (V. Kaufmann, Ber. 1897, 30, 386 ; no melting-point given).

1 : 6-Dihydroxynaphthacene quinone forms red needles, the solution in concentrated sulphuric acid is deep red or yellow, according to strength, and fluoresces on addition of boric acid. The potassium salt is very sparingly soluble ; the solution in boiling water is violet.

Dihydronaphthacene is obtained when 3 grms. of dihydroxynaphthacene quinone and 3 grms. of red phosphorus are intimately mixed, stirred with 22 c.c. of hydriodic acid (b.p. 127°) and heated for 3 to 4 hours in a sealed tube at 154°–157°. The residue is extracted with water and crystallised from 50 c.c. of benzene ; the dihydronaphthacene melts at 206°–207° and distils about 400° (Gabriel and Leupold, Ber. 1898, 31, 1276).

1 : 6-Dihydroxynaphthacenequinone gives a *diacetyl* (m.p. 235°) and a *dibenzoyl* (m.p. 334°–339°) derivative (Gabriel and Leupold, Deichler and Weizmann).

7 : 10-**Dichloro**-1 : 6-**dihydroxynaphthacenequinone** $C_{18}H_6Cl_2(OH)_2O_2$ gives a diacetyl derivative of m.p. 265° (Harrop and Weizmann, Chem. Soc. Trans. 1909, 95, 283).

7 : 8 : 9 : 10-**Tetrachloro**-1 : 6-**dihydroxynaphthacenequinone** $C_{18}H_4Cl_4(OH)_2O_2$ (Harrop and Weizmann, *ibid.* 287).

Dinitro - 1 : 6 - **dihydroxynaphthacenequinone** $C_{18}H_6(NO_2)_2(OH)_2O_2$. By passing nitrous fumes into a sulphuric acid solution of the dihydroxy-compound. Gives a *diamino-dihydroxy-naphthacenequinone* on reduction (Deichler and Weizmann, Ber. 1903, 36 2329).

1 : 7- or 1 : 10-**Dihydroxynaphthacenequinone** $C_{18}H_8(OH)_2O_2$. 1′-Hydroxy-3 (or 6)-methoxy-2-β-naphthoylbenzoic acid (m.p. 210°–215°) is obtained by the condensation of methoxyphthalic anhydride with α-naphthol and then heated with concentrated sulphuric acid. Reddish-violet fluorescent solution in concentrated sulphuric acid ; m.p. indefinite, 280°–300° (Bentley, Friedl, Thomas and Weizmann, Chem. Soc. Trans. 1907, 91, 421).

1 : 8 or 1 : 9-**Dihydroxynaphthacenequinone.** By condensing 4-hydroxyphthalic acid with α-naphthol and heating the product with sulphuric acid. Does not melt by 330°. *Diacetyl derivative*, m.p. 227°–228°. 1-*Hydroxy*-8 or 9-*methoxy-naphthacenequinone* melts about 250° (Bentley, Friedl, Thomas and Weizmann, *ibid.* 422).

1 : 4 : 5-**Trihydroxynaphthacenequinone** ?

$C_{18}H_7(OH)_3O_2$

does not melt below 360°. The solutions in cold sodium carbonate and concentrated sulphuric acid are cornflower-blue in colour (Bentley, Friedl and Weizmann, *ibid.* 1907, 91, 1593).

Trihydroxynaphthacenequinones have also been prepared by fusing 1 : 6-dihydroxynaphthacenequinone with alkali (Deichler and Weizmann, Ber. 1903, 36, 725) and by alkaline fusion of the sulphonic acid obtained from 1 : 6-aminohydroxynaphthacene quinone (Bentley, Friedl, Thomas and Weizmann, Chem. Soc. Trans. 1907, 91, 417).

1-**Aminonaphthacenequinone**

$C_{18}H_9(NH_2)O_2$

From hydroxynaphthacene quinone and ammonia ; m.p. 290°–292° (*ibid.* 415).

1-**Amino**-6-**hydroxynaphthacenequinone**

$C_{18}H_8(NH_2)(OH)O_2$

By reduction of the nitro compound (Deichler and Weizmann, Ber. 1903, 36, 2328 ; Orchardson and Weizmann, Chem. Soc. Trans. 1906, 89, 121 ; Bentley, Friedl, Thomas and Weizmann, *ibid.* 1907, 91, 417).

7 : 10-**Dichloro**-1-**hydroxy**-6-**aminonaphthacenequinone** $C_{18}H_6Cl_2(OH)(NH_2)O_2$ (Harrop and Weizmann, *ibid.* 1909, 95, 284).

1-**Anilino**-6-**hydroxynaphthacenequinone**

$C_{18}H_8(NHC_6H_5)(OH)O_2$

and its *acetyl derivative* (Bentley, Friedl, Thomas and Weizmann, *ibid.* 1907, 91, 419).

2 ?-**Nitro**-6 ?-**anilino**-1-**hydroxynaphthacenequinone** $C_{18}H_7(NO_2)(NHC_6H_5)(OH)O_2$ (*ibid.* 420).

7 (or 10)-**Chloro**-10 (or 7)-**anilino**-1-**hydroxynaphthacenequinone**

$C_{18}H_7Cl(NHC_6H_5((OH)O_2$

(Harrop and Weizmann, *ibid.* 1909, 95, 285).

1-Amino-6 : 8 (or 9)-dihydroxynaphthacenequinone $C_{18}H_7(NH_2)(OH)_2O_2$ (*ibid.* 423).

1 : 6-Dianilinonaphthacenequinone

$$C_{18}H_8(NHC_6H_5)_2O_2$$

By the action of aniline on dichloronaphthacene quinone (Gabriel and Leupold, Ber. 1898, 31, 1283).

8 : 9-Dichloro-7 : 10-dianilino-1-hydroxynaphthacenequinone

$$C_{18}H_5Cl_2(NHC_6H_5)_2(OH)O_2$$

(Harrop and Weizmann, Chem. Soc. Trans. 1909, 95, 288).

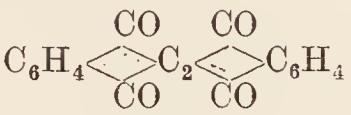
7 : 10-Dianilino-1 : 5-dihydroxynaphthacenequinone $C_{18}H_6(NHC_6H_5)_2(OH)_2O_2$ (*ibid.* 285).

8 : 9-Dichloro-7 : 10-dianilino-1 : 6-dihydroxynaphthacenequinone

$$C_{18}H_4Cl_2(NHC_6H_5)_2(OH)_2O_2$$

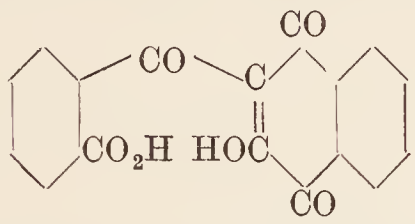
(*ibid.* 288).

Naphthacene-diquinone

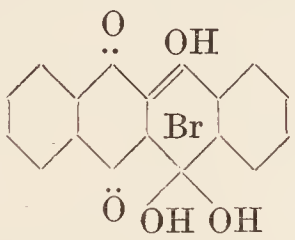


is obtained by the action of nitric acid on 1 : 6-dihydroxynaphthacene quinone. Sinters at 325°, m.p. 330°–333° (Gabriel and Leupold, Ber. 1898, 31, 1283).

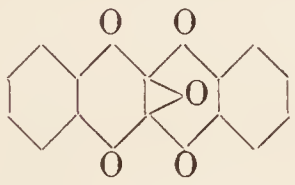
The action of halogens on naphthacene-diquinone has been examined by Voswinckel (Ber. 1905, 38, 4015). The colourless dichloride, $C_{18}H_8O_4Cl_2$, of m.p. 175°, gives the acid



when treated with soda. With bromine, trihydroxynaphthacenequinone bromide



m.p. 198°, is obtained, whilst bleaching powder gives an oxide



melting about 240°.

Voswinckel draws attention to the fact that several compounds which have been described at different times belong probably to the naphthacenequinone series (*e.g.* dibenzoylsuccinic dianhydride, L. Knorr and Scheidt, Annalen, 1896, 293, 74).

1 : 2-Chrysoquinone $C_{18}H_{10}O_2$. By oxidation of chrysene with chromic acid (Liebermann, Annalen, 1871, 158, 309; Graebe, Ber. 1874, 7, 784; Bamberger and Burgdorf, *ibid.* 1890, 23, 2437; Schmidt, J. pr. Chem. 1874, [ii.] 9, 284; Graebe and Hönigsberger, Annalen, 1900, 311, 262). Crystallises in needles from toluene and benzene or in plates from hot glacial acetic acid; m.p. (corr.) 239·5°. *Monooxime*, m.p. 160°–161° (Graebe and Hönigsberger).

The reactions of chrysoquinone resemble those of phenanthraquinone. Derivatives have been described by Liebermann (*l.c.*); Adler (Ber. 1879, 12, 1892); Japp and Streatfeild (Chem. Soc. Trans. 1882, 41, 157) and Abegg (Ber. 1891, 24, 953).

2 : 8- or *amphi*-Chrysoquinone. By oxidising 2 : 8-dihydroxychrysene in boiling glacial acetic acid with lead peroxide. Reddish-yellow needles, m.p. 288°–290°. *Compound*

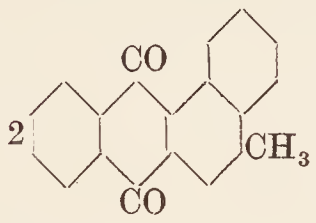
$$C_{18}H_{10}O_2{\cdot}NaHSO_3{\cdot}2H_2O$$

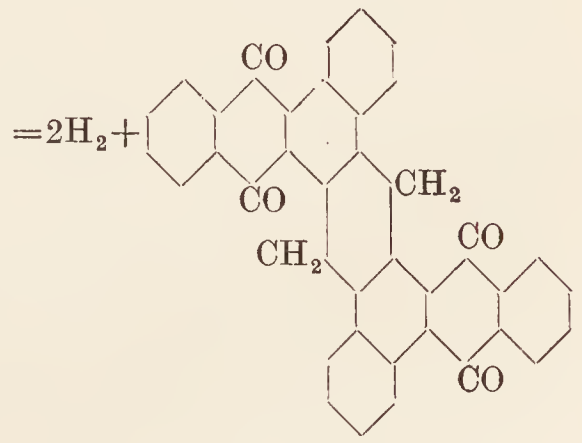
Oxidised by air in hot alcoholic suspension to 8-hydroxy-1 : 2 chrysoquinone, dark-red needles which decompose above 300°. Gives 8-hydroxy-1 : 2-chrysoquinone-1-phenylimine, m.p. 230°, on treatment with aniline (Beschke and Diehm, Annalen, 1911, 384, 173).

Benzanthraquinone $C_6H_4<^{CO(1)}_{CO(2)}>C_{10}H_6$.

From naphthoyl-*o*-benzoic acid and concentrated sulphuric acid. Constitution, Gabriel and Colman (Ber. 1900, 33, 449). *Mononitroderivatives*, &c. (R. Scholl, *ibid.* 1911, 44, 2370, 2992; Monatsh. 1912, 33, 507).

5-Methyl-1 : 2-benzanthraquinone, yellow needles, m.p. 176°–177° (Scholl and Tritsch, Monatsh. 1911, 32, 977), is obtained from 4′-methyl-α-naphthoylbenzoic acid, which is made by the condensation of phthalic anhydride with 1-methylnaphthalene under the influence of aluminium chloride. Heated with alkali and a little anhydrous sodium acetate 1 : 2 : 1′ : 2′ dibenzanthraflavone is produced.





The latter compound gives a vat with alkali and sodium hyposulphite, which dyes unmordanted cotton yellow.

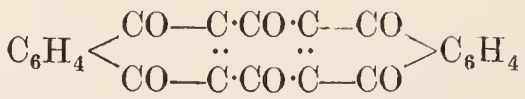
Quinones $C_nH_{2n-32}O_2$

Dinaphthanthraquinone

$$C_{10}H_6<^{(2){\cdot}CO{\cdot}(2)}_{(3){\cdot}CO{\cdot}(3)}>C_{10}H_6$$

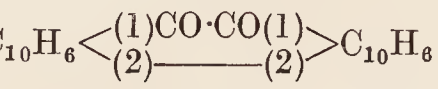
m.p. 388°–389°. By oxidising tetrahydrodinaphthanthracene with anhydrous ferric chloride in glacial acetic acid solution. Flattish, yellow needles, soluble in concentrated sulphuric acid, the solution is blue by transmitted, crimson by reflected light (Mills and Mills, Chem. Soc. Trans. 1912, 101, 2206).

Dinaphthanthratriquinone



obtained by the action of concentrated sulphuric acid on 1 : 4-dihydroxy-3-naphthoic acid (Russig, J. pr. Chem. 1900, [ii.], 62, 30).

Picene-quinone $C_{22}H_{12}O_2$, or



By oxidation of picene, $C_{22}H_{14}$, with chromic acid in acetic acid solution (Burg, Ber. 1880, 13, 1836 ; Bamberger and Chattaway, Annalen, 1895, 284, 64). Red crystalline powder, sublimes (with partial decomposition) as red needles and leaflets. Distilled with soda-lime, picene and $\beta\beta$-dinaphthyl are produced.

Crackene-quinone $C_{24}H_{16}O_2$, m.p. 208°. By oxidation of crackene with chromic acid in acetic acid solution (Klaudy and Fink, Monatsh. 1900, 21, 131).

Quinone $C_nH_{2n-38}O_2$.

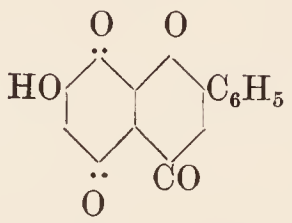
Quinone $C_{32}H_{26}O_2$, m.p. 180°. By oxidising the hydrocarbon $C_{32}H_{28}$ (Carnelly, Chem. Soc. Trans. 1880, 37, 713).

Quinone $C_nH_{2n-40}O_2$.

Dibenzhydryl-*p*-benzoquinone $C_{32}H_{24}O_2$ has already been described.

Quinones from Heterocylic Compounds.

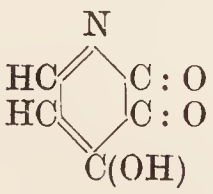
Chrysone



m.p. above 360°. By oxidation of chrysine. *Acetyl derivative*, m.p. 324°–326° (Nierenstein, Ber. 1912, 45, 499).

18-**Hydroxy-2 : 3-quinoxanthone.** From euxanthone. Dark red needles, blue solution in alkalies, red in concentrated sulphuric acid (Nierenstein, Ber. 1913, 46, 649; Chem. Soc. Trans. 1920, 117, 802). Compare Van Scherpenberg, Chem. Weekblad, 1919, 16, 1146.

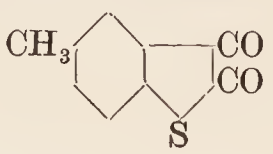
Pyromecazone possibly has the constitution



(Peratoner, Gazz. chem. ital., 1911, 41, ii. 619).

Pyrrindoquinones. By condensation of pyrrole-β-carboxylic acids (Piloty, Wiler and Blömer, Annalen 1914, 407, 1).

Methylthionaphthenequinone



red leaflets, m.p. 144°. From *p*-tolyl mercaptan and oxalyl chloride (Stollé, Ber. 1914, 47, 1130).

A number of compounds may be regarded as possessing the essential structure of quinones, thus maleic anhydride stands in the same relationship to furan as ordinary quinone to benzene. Attention has been drawn to this particular case by Pfeiffer and Böttler (Ber. 1918, 51, 1819).

Intermediate Quinones.

Quinones have been described in which both carbonyl groups are members of one ring ; it will have been noticed that the two carbonyl groups may belong to different rings ; although parts of the same nucleus, as in the cases of *amphi*-naphthaquinone and *amphi*-chrysenequinone. A few other quinones of such type are known.

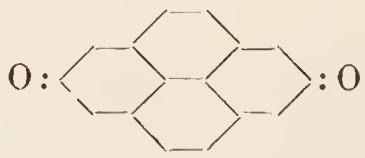
Fluorene-quinone $C_{13}H_8O_2$, is obtained together with diphenylene-ketone, $C_{13}H_8O$, when fluorene is oxidised by chromic acid in acetic acid solution ; m.p. 181°–182° (Barbier, Ann. Chim. 1876, v. 7, 500). Possibly a substance obtained by Behr and van Dorp (Ber. 1874, 7, 399) in small quantity by distilling phenol with 5 parts of litharge is identical with fluorene quinone.

Methylenebiphenylquinones, melting at 280°–281° and 276°–278° respectively, have been described by Carnelly (Chem. Soc. Trans. 1880, 37, 709).

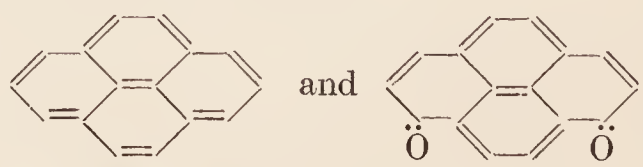
Pyrene-quinone $C_{16}H_8O_2$. By the oxidation of pyrene with chromic acid (Graebe, Annalen, 1871, 158, 295 ; Bamberger and Philip, *ibid.* 1887, 240, 166 ; Goldschmiedt, Monatsh. 1883, 4, 310). A mixture of 10 grms. of pyrene, 15 grms. of potassium dichromate and 110 grms. of sulphuric acid diluted with 5 times its volume of water is heated until a reaction sets in. When apparently over, the mixture is boiled 1 hour longer. Then precipitate with water and digest with dilute sodium carbonate solution some hours at 50°. The residue is recrystallised from acetic acid until free from pyrene. Melts and decomposes about 282°. Soluble in sodium bisulphite solution. Reduced to dihydroxypyrene by boiling with zinc-dust and ammonia.

Dibromo and *tribromo derivatives* (Goldschmiedt).

In place of the constitution

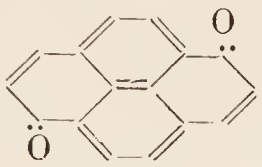


assigned to pyrene quinone by Bamberger and Philip (*l.c.* 158). Goldschmiedt considers that pyrene and its quinone should be represented by the respective formulæ



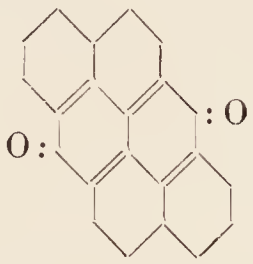
(Annalen, 1907, 351, 258).

Scholl and Seer consider it to have the constitution



(Monatsh. 1912, 33, 1).

Anthanthrone

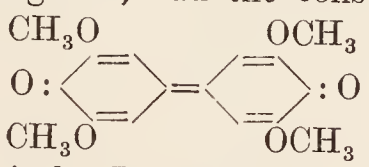


orange yellow needles, m.p. above 300°, is obtained by intramolecular condensation of 1 : 1′-dinaphthyl-2 : 2′-dicarboxylic acid (Kalb, Ber. 1914, 47, 1724).

Heteronuclear Quinones.

Derivatives of Diphenyl.

The earliest known quinone of the diphenyl series, coerulignone, had the constitution



assigned to it by Liebermann (Annalen, 1873, 169, 221; Ber. 1872, 5, 746; 1873, 6, 781; Liebermann and Flatau, *ibid.* 1897, 30, 234; Liebermann and Cybulski, *ibid.* 1898, 31, 615). The parent substance, diphenoquinone, was not isolated until 1905, despite the earlier efforts of Magatti (*ibid.* 1879, 12, 1863; 1880, 13, 224); who obtained the tetrabromo-derivative by the action of nitric acid on tetrabromo-diphenol. The reaction has been further studied by Hunter and Woollett (J. Amer. Chem. Soc. 1921, 43, 149), who have also examined the removal of silver halide from the silver salts of 2 : 4 : 6-trihalogenated phenols (*see* also Kammerer and Benzinger, Ber. 1878, 11, 557). 'Lautermann's Red,' the compound obtained by adding iodine to a solution of phenol in aqueous sodium carbonate and boiling, is tetraiododiphenoquinone (K. and B.; *see* also Bougault, J. Pharm. Chim. 1908, vi. 28, 145; Wilkie, J. Soc. Chem. Ind. 1911, 30, 398; Hunter and Woollett, J. Amer. Chem. Soc. 1921, 43, 131; Vortmann, Ber. 1923, 56, 234).

4 : 4′-Diphenoquinone $O : C_6H_4 : C_6H_4 : O$. Obtained by shaking 10 grms. of *p*-diphenol dissolved in 1 kilo. of ether for one day with 100 grms. of lead peroxide. Two varieties; these crystallise from benzene in thick crystals resembling chromic acid and brighter coloured fine needles respectively. Easily reduced to diphenol, even by phenylhydrazine at the ordinary temperature; liberates iodine from an acidified solution of potassium iodide (Willstätter and Kalb, Ber. 1905, 38, 1232).

Diphenoquinhydrone $C_{24}H_{18}O_4$ gives a cornflower-blue solution in concentrated sulphuric acid and yields a beautiful violet sodium salt.

Diphenoquinone-diimine

$$NH : C_6H_4 : C_6H_4 : NH$$

By oxidising benzidine in indifferent solvents with silver oxide or lead peroxide the di-imine of diphenoquinone is probably first formed; it polymerises, however, to

$$NH_2C_6H_4 \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot C_6H_4NH_2$$

(Willstätter and Kalb, Ber. 1905, 38, 1238; 1906, 39, 3474).

Diphenoquinone dimethyldiimonium platinichloride $C_{14}H_{16}N_2Cl_6Pt + H_2O$, forms beautiful golden brown prisms. It is obtained by addition of chloroplatinic acid to a solution of the green chloride $C_{14}H_{17}ON_2Cl$, obtained from a solution of dimethylbenzidine in dilute hydrochloric acid and excess of ferric chloride (Willstätter and Kalb, Ber. 1904, 37, 3774; compare Willstätter, *ibid.* 1908, 41, 3250).

Diphenoquinone-tetramethyldiimonium bisulphate

$$HSO_4(CH_3)_2N{:}C_6H_4{:}C_6H_4{:}N(CH_3)_2SO_4H + 2H_2O$$

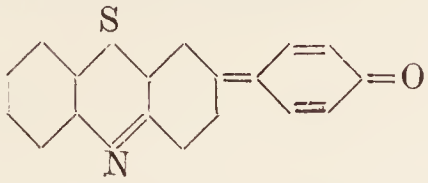
separates in red prisms, which appear blue or violet by reflected light, when excess of chlorine or nitrous acid is led into a solution of 1 grm. of tetramethylbenzidine in 10 c.c. of 30 p.c. sulphuric acid and 50 c.c. of 96 p.c. alcohol (Willstätter and Kalb, Ber. 1904, 37, 3768). The *chloride* is too deliquescent to analyse but the *platinichloride* $C_{16}H_{20}N_2Cl_6Pt + 2H_2O$ and the *periodide* $C_{16}H_{20}N_2I_4$, have been isolated. Solutions of the salts are intensely orange-yellow; alkalies first give green solutions of a compound of meriquinonoïd type and decomposition then ensues. With sulphurous acid, tetramethylbenzidine monosulphonic acid is produced (compare Willstätter and Piccard, Ber. 1908, 41, 1466, 3250).

Diphenoquinone dichlorodiimine $C_{12}H_8N_2Cl_2$, chocolate brown amorphous powder, explodes at 135°, or red needles which explode at 155°–160° (Schlenk, Knorr and Keller, Annalen, 1908, 363, 313; 1909, 368, 271).

Resorcinol and halogens yield trihalogen substituted resorcinols; further action of halogen yields derivatives of diphenyl which are probably quinones of the 4 : 4′-series (Zincke and Schwabe, Ber. 1909, 42, 797).

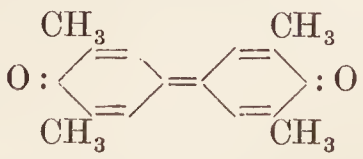
Orthodiphenol appears to be incapable of giving a quinone (Ber. 1905, 38, 1233 footnote); but Schlenk, Knorr and Keller (*l.c.*) have described the *dichlorodiimine* of the 2 : 4′-*quinone*, $ClN : C_6H_4 : C_6H_4 : NCl$, as a light brown amorphous powder which explodes on heating.

***o* : *o*-Thiodipheno-quinoneanil**



m.p. 150°, is obtained by oxidising a mixture of thiodiphenylamine and aniline with yellow mercuric oxide (Pesci, Gazz. chim. ital. 1916, 46, i. 103).

Tetramethyldiphenoquinone



By adding a solution of 1½–2 times the theoretical amount of chromic anhydride dissolved in strong acetic acid to a hot solution of

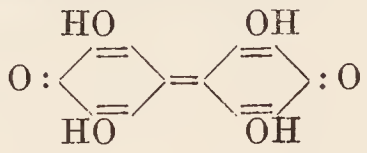
vic. *m*-xylenol in 50 times its weight of glacial acetic acid. Dark red crystals, bluish reflex, m.p. 207°–217°, according to rapidity of heating. Yellowish-brown solution in concentrated sulphuric acid; oxidising agent (Auwers and von Markovitz, Ber. 1905, 38, 226).

Dihydroxy- and dimethoxy-diphenoquinone are unknown, but the quinhydrone of dianisidine with 3 : 3′-dimethoxy-diphenoquinonediimine, $C_{218}H_{32}O_4N_4Cl_2$ appears to be formed by oxidation of dianisidine with ferric chloride (Moir, South African J. Sci. March, 1914).

3 : 3′-*Dimethyl*-5 : 5′-*dihydroxy*-4 : 4′-*diphenoquinone*. A ferrous salt of this compound is obtained by the action of ferric chloride on an aqueous solution of 2 : 3-dihydroxytoluene in the cold (Majima and Takayama, Ber. 1920, 53, 1937).

3 : 3′-*Dimethyl*-5 : 5′-*dimethoxy*-4 : 4′-*diphenoquinone* is obtained by the oxidation of an alcoholic solution of 3-methoxy-*o*-cresol with ferric chloride. Dark violet needles, m.p. 202°–203° (Majima and Takayama).

Tetrahydroxydiphenoquinone



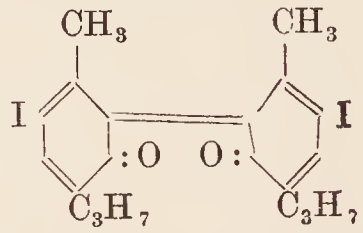
By oxidising an aqueous solution of hexahydroxydiphenyl with an alcoholic solution of iodine (Liebermann and Bung, Ber. 1876, 9, 1887; Liebermann and Herrmuth, Ber. 1912, 45, 1218). Microscopic blue needles, blue solution in alkalis. The necessary hexahydroxy-diphenyl is obtained from the reduction product of coerulignone by hydrolysis with hydrochloric acid (Liebermann, Annalen, 1873, 169, 239). The *dimethyl* and *trimethyl* ethers have been obtained by partial hydrolysis of coerulignone.

Tetramethoxydiphenoquinone (Cedriret or Coerulignone), $O{:}C_6H_2(OCH_3)_2{:}C_6H_2(OCH_3){:}O$. By treating an acetic acid solution of pyrogallol-dimethyl ether (occurs in beech and birch tars) with potassium dichromate. The ether may also be oxidised by ferric chloride, chlorine, iodine or nitric acid (Hofmann, Ber. 1878, 11, 335). The production of coerulignone by addition of potassium dichromate to crude acetic acid obtained by distilling wood is easily explicable (Liebermann, Annalen, 1873, 169, 231). The coerulignone which separates on standing some days is dissolved in phenol (not above 30°) and precipitated by alcohol. Dark steel blue needles, insoluble in most organic solvents, soluble in concentrated sulphuric acid with cornflower-blue colour. By addition of water to the sulphuric acid solution, the *di-* and *tri-methyl ethers* of diphenoquinone are precipitated. Decomposed by alkalis, reducing agents furnish hydrocoerulignone (tetramethoxydiphenol).

Coerulignone yields dyes when heated with aromatic amines; two molecular proportions of the latter are employed (Akt. Ges. Anilin-F., D. R. P. 94503, 1897). As an example, 10 parts of coerulignone are heated with 8 parts of *p*-toluidine and 120 parts of glacial acetic acid. The reaction begins at once, the solution becoming a beautiful blue; the reaction is finished in 15 minutes. Most of the dyestuff can be filtered off from the cold solution, the remainder may be recovered by precipitation with water. Various amines as well as their amino-carboxylic and sulphonic acids, may be employed. Friedländer (Fortschritte der Theerfarbenfabrikation, iv. 1060) states that the quinone-anilide dyes obtained in this manner are too unstable for practical application. For the action of amines on coerulignone compare Liebermann (Ber. 1897, 30, 234, 3137; 1898, 31, 615).

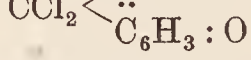
Tetraethoxydiphenoquinone or ethyl coerulignone, $C_{20}H_{24}O_6$ (Hofmann, Ber. 1878, 11, 801). A compound $C_{20}H_{24}O_6HNO_3$ separates as purple needles on leading nitrous fumes into an ethereal solution of pyrogallol diethyl ether. Hydrolyses immediately by water (Weselsky and Benedikt, Monatsh. 1881, 2, 215).

Besides 4 : 4′-diphenoquinone, isomeric 2 : 4′- and 2 : 2′-compounds are theoretically possible. Perhaps aristol, the product of the action of iodine on thymol (Messinger and Vortmann, Ber. 1889, 22, 2312), is such a compound. Bougault (J. Pharm. Chim. 1918, 17, 221) has assigned to it the structure



(Compare Moles and Marquina, Anal, fis. quim. 1919, 17, 59, and Woollett, J. Amer. Chem. Soc. 1921, 43, 553.)

9 : 9-**Dichloro**-2 : 7-**fluorenequinone**,

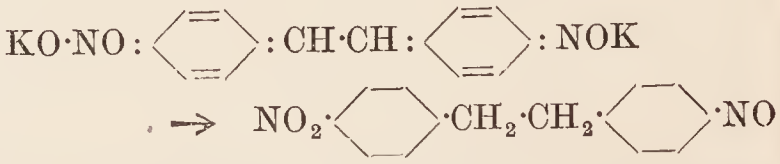


yellow needles, m.p. 165°, is obtained by heating 2 : 7 : 9 : 9-tetrahydroxyfluorene with phosphorus pentachloride to 250° (Schmidt, Retzloff and Haid, Annalen, 1912, 390, 210).

Derivatives of Stilbene.

Stilbenequinone $O : C_6H_4 : CH{\cdot}CH : C_6H_4 : O$. Obtained by the action of ferric chloride on *pp′*-dihydroxystilbene in presence of calcium carbonate (Zincke and Fries, Annalen, 1902, 325, 19; Zincke and Münch, *ibid.* 1904, 335, 157); or by shaking a suspension of 2 grms. of dihydroxystilbene in 500 c.c. ether for several hours with 25 grms. of lead peroxide. Extracted by benzene from its mixture with the lead oxides; m.p. 284°. Reduced to dihydroxystilbene by phenylhydrazine (Willstätter and Benz, Ber. 1906, 39, 3490; *see* also Zincke and Münch, *l.c.*).

Nitroximes and *oximes* of stilbenequinone exist as alkaline salts; the free compounds pass over, however, into dibenzyl derivatives, *e.g.*



(A. G. Green, Ber. 1897, 30, 3097; Chem. Soc. Trans. 1904, 85, 1424, 1432; 1907, 91, 2076; 1908, 93, 1721).

Tetrabromostilbenequinone

$O : C_6H_2Br_2 : CH{\cdot}CH : C_6H_2Br_2 : O$

Dihydroxystilbene and bromine yield tetrabromodi-*p*-hydroxydibenzyl ψ-bromide (tetrabromo-di-*p*-hydroxystilbene dibromide), m.p. 265°, which, boiled with acetone, gives the quinone. Also obtained by oxidising 3 : 5 : 3′ : 5′-terabromo-4 : 4′-dihydroxystilbene with nitric acid. Red powder or steel blue needles from nitrobenzene, changes to a pale yellow at 300° (Zincke and Fries, *l.c.*).

2 : 5 : 2′ : 5′-Tetrabromo-3 : 3′-dimethylthiolstilbene-4 : 4′-quinone

$O{:}C_6HBr_2(SCH_3){:}CH{\cdot}CH{:}C_6HBr_2(SCH_3){:}O.$

By the action of solid sodium acetate on an ethereal solution of 2 : 5-dibromo-3-methylthiol-*p*-cresol ψ-bromide. Deep black powder, m.p. 240° with decompostion (Zincke and Kempf, Ber. 1911, 44, 413; Zincke, Frohneberg and Kempf, Annalen, 1911, 381, 28).

Derivatives of Azobenzene.

Azobenzenequinone, or quinone azine

$$O : C_6H_4 : N{\cdot}N : C_6H_4 : O.$$

By shaking a solution of 5 grms. of hydrated *p*-azophenol $HO{\cdot}C_6H_4{\cdot}N : N{\cdot}C_6H_4{\cdot}OH$, dissolved in 1 litre of ether with silver oxide (obtained from 15 grms. of silver nitrate) and 10 grms. of ignited sodium sulphate. About 2 grms. of the quinone-azine may be obtained by evaporating the ether, the yield can be raised to 90 p.e. of the theoretical by boiling out the silver mud with three portions each of 100 c.c. of chloroform and evaporating the solvent. Purified by recrystallisation from ethyl acetate (Willstätter and Benz, Ber. 1906, 39, 3486). Crystallises either as dark orange-red prisms, giving a brick-red powder, or in dark yellow leaflets, powder yellow. Explodes at 158°. The solutions are deeper coloured than those of azophenol. Liberates iodine from acidified potassium iodide. Partial reduction gives the *quinhydrone*

$$C_{24}H_{18}O_4N_4,$$

m.p. 181°–182°, the same compound is obtained by mixing equimolecular quantities of the quinone-azine and azophenol in ethereal solution. Stronger reducing agents (*e.g.* aluminium amalgam, zinc-dust and water, stannous chloride and hydrochloric acid) give an azophenol not identical with the azophenol from which the quinone-azine was prepared (Willstätter and Benz, Ber. 1906, 39, 3492).

Addition Compounds of Quinones.

(Meriquinonoïd Compounds.)

A large number of substances are known in which quinonoïd and benzenoïd compounds have entered into a somewhat loose combination. The earliest-known member of this group was *quinhydrone*, a strongly coloured equimolecular compound of quinone and quinol discovered by Wöhler in 1844 (Annalen, 51, 153). The term quinhydrone is now used generically for the addition products of quinones and phenols, but since similar addition products of quinone-diimonium salts with aromatic diamines are also known which are likewise intensely coloured, Willstätter has introduced the term *meriquinonoïd* to include all compounds formed by addition of quinonoïd and benzenoïd molecules (Willstätter and Piccard, Ber. 1908, 41, 1458).

The relationships between quinone, quinol, and quinhydrone were obscured for some time, owing to the last being produced as an intermediate compound during the conversion of quinone into chloroquinol by addition of hydrogen chloride (Staedeler, Annalen, 1849, 69, 308). Quinhydrone is, however, undoubtedly an addition product, for besides the methods of preparation used by Wöhler, viz. the incomplete oxidation of quinol or the incomplete reduction of quinone, it is also formed by the combination of quinone and quinol $C_6H_4O_2+C_6H_4(OH)_2=C_{12}H_{10}O_4$ and may be resolved into its constituents by boiling with water, the quinone volatilising and the quinol remaining in solution. Quinone generally combines with two molecules of a monatomic phenol, or with one of a diatomic phenol, although Wichelhaus at one time held the view that quinhydrone itself contained two molecules of quinol to one of quinone (Ber. 1872, 5, 849; 1879, 12, 1500). This idea was negatived by the work of Liebermann (*ibid.* 1877, 10, 1614). Nietzki (*ibid.* 2003; Annalen, 1882, 215, 125) and Hesse (*ibid.* 1880, 200, 232).

The quinhydrones and other meriquinonoïd compounds in common with many deeply coloured inorganic substances (*e.g.* sulphur sesquioxide, Prussian blue, &c.), have a constituent present in two distinct stages of oxidation. In the meriquinoïd compounds, a dynamical equilibrium is supposed to exist between two or three molecules or benzene nucleï, similar to the intramolecular dynamical equilibrium, which, under the name of *isorrhopesis*, has been employed by Baly to furnish an explanation of the absorption of various carbonyl-compounds (*see* Chem. Soc. Trans. 1904, 85, 1029; 1905, 87, 766; 1332, 1347, 1355; 1906, 89, 502, 514, 966, 982; 1907, 91, 1572; 1908, 93, 1747, 1806, 1902; 1909, 95, 144, 1096).

Whilst the quinhydrones are formed by the addition of quinones and phenols, the formation of quinhydrone as an intermediate product when hydrogen chloride is passed into a solution of quinone still has to be explained, especially in view of the fact that with a sufficient amount of hydrogen chloride a practically quantitative yield of chloroquinol is obtained. Wichelhaus, finding that quinone oxidises substituted quinols to substituted quinones whilst it is itself reduced to quinol, offered as an explanation that quinol liberates chlorine from hydrogen chloride which then acts upon quinol.

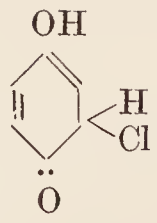
$$C_6H_4O_2+2HCl=C_6H_4(OH)_2+Cl_2$$
$$C_6H_4(OH)_2+Cl_2=C_6H_3Cl(OH)_2+HCl.$$

The production of chlorine appears improbable. Thiele's theory (Annalen, 1899, 306, 133) obviates this difficulty, but does not account for the intermediate production of quinhydrone (*see* Michael, J. pr. Chem. 1903, 68, 509; 1909, 79, 423; Posner, Annalen, 1904, 336, 109). Michael and Cobb (J. pr. Chem. 1910, 82, 298) assume the production of a complex

$$2C_6H_4O+HCl,$$

which decomposes giving nascent chlorine, the latter acts as a substituting agent on quinone instead of being directly added.

Posner supposes an addition product



is first formed and is then oxidised to chloroquinone which with quinol gives a substituted quinhydrone. The latter compound and hydrogen chloride give two molecules of chloroquinol (J. pr. Chem. 1911, ii. 83, 478).

Schmidlin (Ber. 1911, 44, 1700) considers Thiele's theory sufficient. The first action of hydrogen chloride is to furnish chloroquinol, which establishes an equilibrium with quinone, quinol and chloroquinone in the following sense :

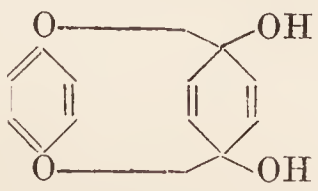
$$O{:}C_6H_4{:}O + HO{\cdot}C_6H_3Cl{\cdot}OH \rightleftharpoons HO{\cdot}C_6H_4{\cdot}OH + O{:}C_6H_3Cl{:}O$$

This view is supported by the observations of Wichelhaus (Ber. 1879, 12, 1503), Biltris (Bull. Acad. roy. Belge, 1898, iii. 35, 44), and Valeur (Ann. Chim. Phys. 1900, vii. 21, 551), and explains the separation of non-substituted quinhydrone on adding hydrogen chloride to a solution of quinone in insufficient amount to effect complete conversion into chloroquinol. The solution will contain an equilibrium mixture of two quinones and two quinols, from which the least soluble (the unsubstituted) quinhydrone separates.

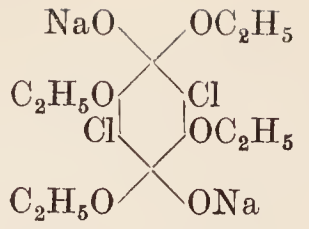
The observation of Ling and Baker (Chem. Soc. Trans. 1893, 63, 1314) that each of the two chloroquinhydrones (m.p. 138°–142° and 132°–133° respectively) give the sparingly soluble non-substituted quinhydrone and the more soluble dichloroquinhydrone on boiling with petroleum ether, is also easily explained, the quinhydrones being largely dissociated into their constituents in solution.

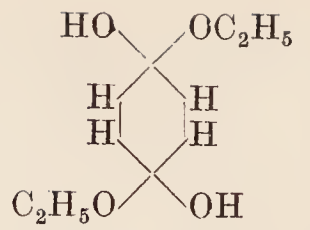
The quinhydrones and other meriquinonoïd compounds result from direct addition of quinonoïd and benzenoïd substances, and the question of the manner in which the two kinds of molecules are linked requires consideration.

In accordance with the peroxide formula for quinone, Graebe (Annalen, 1868, 146, 61) formulated quinhydrone as $HO{\cdot}C_6H_4{\cdot}O{\cdot}O{\cdot}C_6H_4{\cdot}OH$. A corresponding formula based on the diketonic formula for quinone is



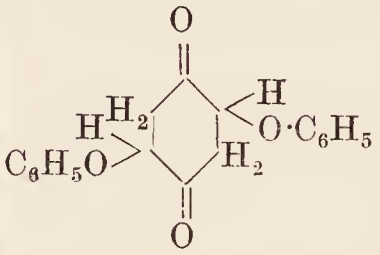
(C. Loring Jackson and Oenslager, Ber. 1895, 28, 1614), though it might be objected that a compound of such a constitution would hardly show selective absorption in the visible spectrum, whilst quinhydrone is actually a strongly-coloured substance. Jackson and Oenslager started out from the fact that dichlorodiethoxyquinone combines with two molecules of sodium ethoxide (Jackson and Grindley, Proc. Amer. Acad. 1894, 30, 409) and assumed that the salt was of hemiacetal type and corresponded to phenoquinone, the compound produced by the union of one molecule of quinone with two molecules of phenol.



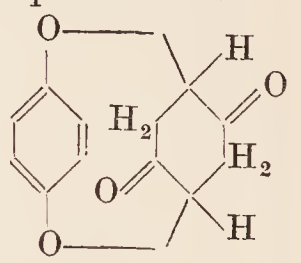


Jackson and Oenslager point out that their theory requires the union of one molecule of quinone with one molecule of a dihydric phenol such as quinol or resorcinol or with two molecules of phenol or the monomethyl ether of quinol, whilst the dimethyl ether of quinol should not react. The facts agree with these requirements except that Schlenk and Knorr have recently prepared an addition product of one molecule of dimethyl quinol ether with one molecule of quinone, and the production of diacetylquinol and quinone from quinhydrone and acetic anhydride (Hesse, Annalen, 1880, 200, 249), which Nietzki regarded as a proof of the absence of hydroxyl groups, is considered by Jackson and Oenslager to be a further argument in favour of their formula.

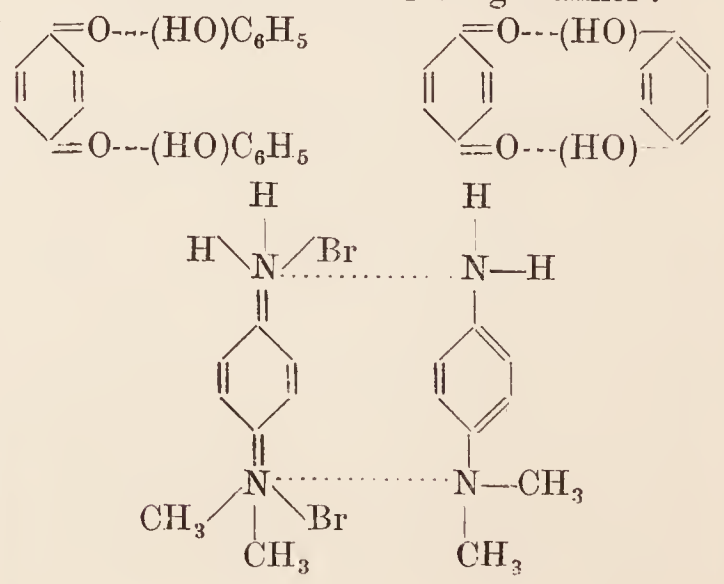
What may be designated as a 'phenol-ether' formula has been advocated by A. Valeur (Thèse, Paris, 1900); Gauthier-Villars (Ann. Chim. Phys. 1900, [vii.] 21, 546) and Th. Posner (Annalen, 1904, 336, 85); thus phenoquinone and quinhydrone may be respectively represented as



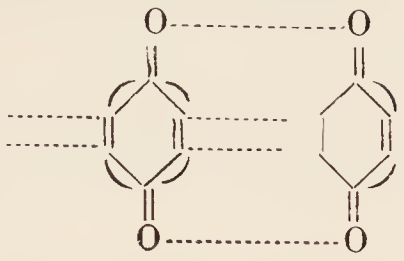
and



Willstätter and Piccard (Ber. 1908, 41, 1458) point out that none of these formulæ takes into account the deep colour and the easy dissociability of the quinhydrones (compare H. A. Torrey and H. Hardenbergh, Amer. Chem. J. 1905, 33, 167), and having discovered that the salts of bases obtained by Wurster by the oxidation of *p*-diamines (Ber. 1879, 12, 1803, 1807, 2071; 1886, 19, 3195, 3217) were only half quinonoïd, decided that the quinhydrones and Wurster's compounds belong to one category, residual affinity effecting a loose combination between the quinone or quinonoïd salt and the phenol or aromatic base. Quinhydrone is largely dissociated in aqueous solution. For quinone × quinol/quinhydrone K = 0·23 at 25° (Luther and Leubner, J. pr. Chem. 1912, [ii.] 85, 314). Phenoquinone, quinhydrone and Wurster's red (the product of the action of bromine on dimethyl-*p*-phenylenediamine) are then formulated in the following manner :



A somewhat similar idea is to found in formulation of quinhydrone as



(G. Urban Monatsh. 1907, 28, 299); Willstätter and Piccard (*l.c.*) 1464, footnote, point out that this does not take into account the salt formation of the quinhydrones.

Pfeiffer (Annalen, 1914, 401, 1) looks on the quinhydrones as derived from parent substances such as

$$O : C_6H_4 : O \ldots\ldots\ldots\ldots C_6H_6$$

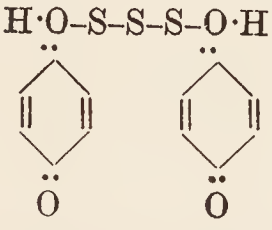
and $$C_6H_6 \ldots\ldots O : C_6H_4 : O \ldots\ldots\ldots C_6H_6$$

the hydrocarbon, phenol or ether being co-ordinatively linked to the carbonyl group. Substances of the type formulated above function as chromogens, and by introduction of auxochromic hydroxyl or amino groups, the intensely coloured quinhydrones are formed. The relationship to the coloured compounds formed by ketones with salts and acids, *e.g.*

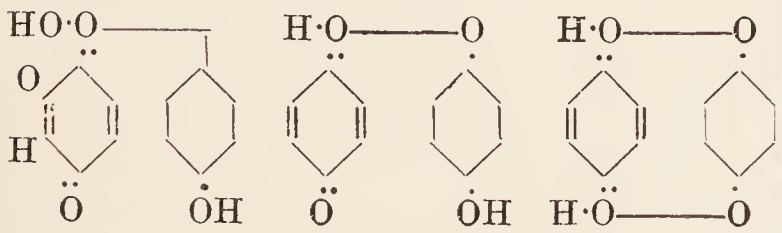
$$R_2CO \ldots\ldots SnCl_4, \quad R_2CO \ldots\ldots HCl$$

is thus emphasised.

M. M. Richter, who formulates the addition product of hydrogen persulphide and quinone as



thinks the quinhydrones are also oxonium compounds. Three oxonium formulæ



are possible for ordinary quinhydrone of which the second is preferred (Ber. 1910, 43, 3603). This view does not commend itself to Angelo Knorr (*ibid.* 1911, 44, 1503). The true immonium compound obtained from quinone-diimine and *p*-nitrophenol (m.p. 59°) is yellow, *i.e.* has not the marked colour associated with quinhydrones.

The quinhydrones have been spectrographically examined (Lifschitz, Ber. 1916, 49, 2050).

The meriquinonoïd compounds obtained from bases were frequently mistaken for the quinonoïd substances themselves.

Jackson and Calhane acted on *p*-phenylene-diamine and its dibromo-derivative with bromine, obtaining deeply coloured salts which they considered were compounds of the diimines

$$C_6H_4(:NH)_2 \text{ and } C_6H_2Br_2(:NH)_2$$

(Ber. 1902, 35, 2495). Subsequently it was found that quinone-imine and quinone-diimine were colourless substances and gave colourless salts if in a state of purity (Willstätter and Pfannenstiehl, Ber. 1904, 37, 4606). Kehrmann suggested that many of the deeply coloured oxidation products obtained from simple amines might be of quinhydrone type (*ibid.* 1905, 38, 3777). A careful examination by Willstätter and Piccard (*ibid.* 1908, 41, 1458) of the oxidation products obtainable from dimethyl-*p*-phenylene diamine showed that whilst the completely quinonoïd nitrate

$$HNO_3 \cdot HN : C_6H_4 : N(CH_3)_2NO_3$$

was colourless, the coloured salts obtained by Wurster (Ber. 1879, 12, 1803, 1807, 2071) and considered by Bernthsen (Annalen, 1885, 230, 162; 1889, 251, 11, 49, 82) to be wholly quinonoïd, are actually of meriquinonoïd type. Wurster's red must be considered as an addition product

$$BrNH_2{:}C_6H_4{:}N(CH_3)_2Br + NH_2 \cdot C_6H_4 \cdot N(CH_3)_2$$

Kehrmann (Ber. 1908, 41, 2340), and Schlenk and Knorr both draw attention to the fact that quinhydrones are dissociated into their constituents in solution, but Wurster's red is not. Evidently the firmness of union of quinonoïd and benzenoid molecules varies in degree (Willstätter and Piccard, Ber. 1909, 42, 1902).

Jean Piccard (Annalen, 1911, 381, 351) has shown that the meriquinonediimmonium salts

$$NH_2Br : C_6H_4 : NH_2Br + NH_2 \cdot C_6H_4 \cdot NH_2$$

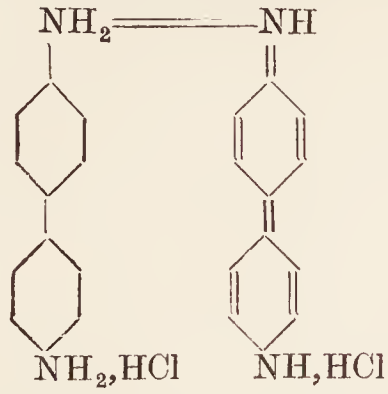
exist in two modifications, α and β. The α-compounds are formed preferably in presence of alcohol; the β-salts, which are polymers and more strongly coloured, at low temperatures, in presence of water. The β-form is usually the more stable. (See also Ber. 1913, 46, 1860.)

Hantzsch (Ber. 1916, 49, 511) suggests tentatively that the meriquinonoïd salts may be simple unsaturated compounds, *e.g.* Wurster's salt may be



The intense colour might then be attributed to unsaturation.

G. Woker (Ber. 1916, 49, 2319) prefers regarding the meriquinonoïd oxidation product of benzidine as a compound of one molecule of benzenoid benzidine with a quinone-imine molecule and two molecules of hydrochloric acid



The difference of oxidisability of different benzidine hydrochlorides to meriquinonoïd salt is supposed to be due to the existence of *cis*- and *trans*- 'dibenzidine' salts

$$\begin{matrix} NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2,HCl \\ \| \\ NH_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NH_2,HCl \end{matrix}$$

and

$$HCl,NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$$
$$\|$$
$$NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2,HCl$$

the *cis-* form being the more easily oxidised.

Some of the addition products formed by quinones and quinonoïd compounds are given in the following list. The figures in brackets refer to the number of molecules of reacting substances, *e.g.* :—

(3) 1:4-$C_6H_4O_2$+(4)1:2:3 $C_6H_3(OH)_3$, m.p. 78°, Siegmund,

means that Siegmund has prepared an addition product of 3 molecules of *p*-benzoquinone with 4 molecules of pyrogallol which melts at 78°.

(1)1:4-$C_6H_4O_2$+(2)C_6H_5OH, m.p. 71°, Wichelhaus.
(1)1:4-$C_6H_4O_2$+(2)1:4-$C_6H_4(OCH_3)(OH)$
(1)1:4-$C_6H_4O_2$+(1)1:3-$C_6H_4(OH)_2$, m.p. 90°, Nietzki.
(1)1:4-$C_6H_4O_2$+(1)1:4-$C_6H_4(OH)_2$, m.p. 171°, Wöhler.
(1)1:4-$C_6H_4O_2$+(1)1:4-$C_6H_4(OCH_3)_2$, Schlenk and Knorr.
(1)1:4-$C_6H_4O_2$+(1)2:1:4-$C_6H_3Cl(OH)_2$, m.p. 145°, Ling and Baker.
(3)1:4-$C_6H_4O_2$+(4)1:2:3-$C_6H_3(OH)_3$, m.p. 78°, Siegmund.
(3)1:4-$C_6H_4O_2$+(4)1:2:4-$C_6H_3(OH)_3$, m.p. 164°, Siegmund.
(3)1:4-$C_6H_4O_2$+(2)1:3:5-$C_6H_3(OH)_3$, m.p. 103°, Siegmund.
(1)1:4-$C_6H_4O_2$+(1)2:3-$C_{10}H_6(OH)_2$, m.p. 78°–80°, Siegmund.
(5)1:4-$C_6H_4O_2$+(2)1:4-$C_6H_4(NH_2)_2$, m.p. 83°, Schlenk and Knorr.
(1)1:4-$C_6H_4O_2$+(1)$CH_2(C_6H_4\cdot NH_2)_2$, m.p. 72°–73°, Siegmund.
(1)1:4-$C_6H_4O_2$+(1)$C_2H_2(C_6H_4\cdot NH_2)_2$, m.p. 130°, Siegmund.
(1)1:4-$C_6H_4O_2$+(2)1:4-$NH_2\cdot C_6H_4\cdot CO_2CH_3$, m.p. 83°, Siegmund.
(1)2:1:4-$C_6H_3ClO_2$+(1)1:4-$C_6H_4(OH)_2$, m.p. about 130°, Ling and Baker.
(1)2:1:4-$C_6H_3ClO_2$+(1)2:1:4-$C_6H_3Cl(OH)_2$, m.p. 93°–94°, Wöhler; Ling and Baker.
(1)2:5:1:4-$C_6H_2Cl_2O_2$+(1)2:5:1:4-$C_6H_2Cl_2(OH)_2$, m.p. 140°–145°, Ling and Baker.
(1)2:6:1:4-$C_6H_2Cl_2O_2$+(1)2:6:1:4-$C_6H_2Cl_2(OH)_2$, m.p. 130°, Ling and Baker.
(1)2:5:1:4-$C_6H_2Cl_2O_2$+(1)2:5:1:4-$C_6H_2Br_2(OH)_2$, m.p. 130°–135°, Ling and Baker.
(1)2:3:5:1:4-$C_6HCl_3O_2$+(1)2:3:5:1:4-$C_6HCl_3(OH)_2$, m.p. 109°–110°, Ling and Baker.
(1)2:3:5:6:1:4-$C_6Cl_4O_2$+(1)2:3:5:6:1:4-$C_6Cl_4(OH)_2$, m.p. 160°, Staedeler; Loring Jackson.
(1)*p*-$C_6Cl_4O_2$+(1)1:4-$C_6H_4(NH_2)_2$, Schlenk and Knorr.
(1)*p*-$C_6Cl_4O_2$+(1)1:4-$C_6H_4[N(CH_3)_2]_2$, m.p. 80°, Schlenk and Knorr.
(1)*p*-$C_6Cl_4O_2$+(1)$(CH_3)_2N\cdot C_6H_4\cdot C_6H_4\cdot N(CH_3)_2$, Schlenk and Knorr.
(1)*p*-$C_6Cl_4O_2$+(1)$NH_2\cdot C_6H_2Cl(CH_3)\cdot C_6H_2Cl(CH_3)\cdot NH_2$, Schlenk and Knorr.
(1)*p*-$C_6Cl_4O_2$+(1)$NH_2\cdot C_6H_2Br(CH_3)\cdot C_6H_2Br(CH_3)\cdot NH_2$, m.p. 225–228°, Schlenk and Knorr.
(1)2:1:4-$C_6H_3BrO_2$+(1)2:1:4-$C_6H_3Br(OH)_2$, m.p. 98°, Ling and Baker.
(1)2:5:1:4-$C_6H_2Br_2O_2$+(1)2:5:1:4-$C_6H_2Br_2(OH)_2$, m.p. 145°–150°, Ling and Baker.
(1)2:5:1:4-$C_6H_2Br_2O_2$+(1)2:5:1:4-$C_6H_2Cl_2(OH)_2$, m.p. 135°–140°, Ling and Baker.
(1)*p*-$C_6Br_4O_2$+(1)$(CH_3)_2N\cdot C_6H_4\cdot C_2H_4\cdot N(CH_3)_2$, Schlenk and Knorr.
(1)*p*-$C_6Br_4O_2$+(1)$NH_2\cdot C_6H_2Br(CH_3)\cdot C_6H_2Br(CH_3)\cdot NH_2$, m.p. 190°, Schlenk and Knorr.
(1)2:1:4-$C_6H_3(OH)O_2$+(1)1:2:4-$C_6H_3(OH)_3$, Barth and Schreder.
(1)2:1:4-$C_6H_3(CH_3)O_2$+(1)2:1:4-$C_6H_3(CH_3)(OH)_2$, m.p. 52°, Nietzki.
(1)1:4:2:5-$C_6H_2(CH_3)(C_3H_7)O_2$+(1)1:4:2:5-$C_6H_2(CH_3)(C_3H_7)(OH)_2$, Liebermann.
(1)O:C_6H_4:C_6H_4:O+(1)HO·$C_6H_4\cdot C_6H_4\cdot$OH, Willstätter and Kalb.
(1)1:4-$C_6H_4(:NH)_2$+(1)$NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, m.p. 128°–145°, Schlenk and Knorr.
(1)1:4-$C_6H_4O(:NCl)$+(1)1:4-$C_6H_4(OH)_2$, expl.p. 119°, A. Knorr.
(1)1:4-$C_6H_4(:NCl)_2$+(1)1:4-$C_6H_4(OH)_2$, expl.p. 129°–130°, A. Knorr.
(1)1:4-$C_6H_4(:NCl)_2$+(2)$NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, expl.p. 121°, A. Knorr.
(1)1:4-$BrNH_2$:C_6H_4:$N(CH_3)_2Br$+(1)1:4-$NH_2\cdot C_6H_4\cdot N(CH_3)_2$, Willstätter and Piccard.
(1)$HSO_4\cdot N(CH_3)_2$:C_6H_4:$N(CH_3)_2SO_4H$+(2)1:4-$C_6H_4[N(CH_3)_2]_2$,H_2SO_4, Willstätter and Piccard.
(1)NH:C_6H_4:C_6H_4:NH+(4)$NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$+(4)$H_2CrO_4$, Willstätter and Piccard.
(1)NH:C_6H_4:C_6H_4:NH+(3)$NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$+(5)$H_2CrO_4$, Willstätter and Piccard.
(1)$Cl(CH_3)_2N$:C_6H_4:C_6H_4:$N(CH_3)_2Cl$+(1)$(CH_3)_2N\cdot C_6H_4\cdot C_6H_4\cdot N(CH_3)_2$+(6)$H_2O$, Willstätter and Piccard.
(1)NH:$C_6H_2(CH_3)Cl$:$C_6H_2(CH_3)Cl$:NH+(1)$NH_2\cdot C_6H_2(CH_3)Cl\cdot C_6H_2(CH_3)Cl\cdot NH_2$+(2)HCl, Schlenk and Knorr.

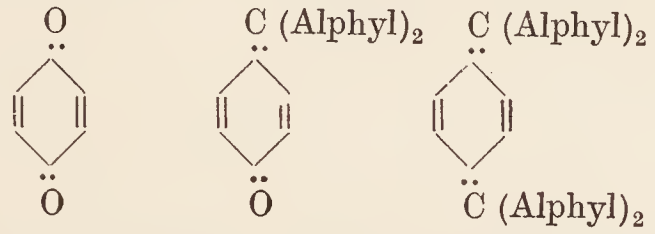
Neither the above list of meriquinonoïd compounds nor the subjoined list of references pretends to be exhaustive. Some idea will be gained, however, of the types of substances which form meriquinonoïd compounds and the molecular proportions in which combination takes place.

Barth and Schreder, Monatsh. 1884, 5, 595; T. H. Clark, Amer. Chem. J. 1892, 14, 574; Graebe, Annalen, 1868, 146, 27; Haack, Ber. 1909, 42, 4595; Hesse, Annalen, 1880, 200, 248; C. L. Jackson and Carleton, Amer. Chem. J. 1908, 39, 493; Klinger and Standke, Ber. 1891, 24, 1340; Angelo Knorr, *ibid.* 1911, 44, 1503; Liebermann, *ibid.* 1877, 10, 1615; Ling and Baker, Chem. Soc. Trans. 1893, 63, 1314; W. Madelung, Ber. 1911, 44, 626; K. H. Meyer, *ibid.* 1910, 43, 157; Nietzki, Annalen, 1882, 215, 130; Ber. 1879, 12, 1982; Piccard, Annalen, 1911, 381, 351; Ber. 1911, 44, 959; M. M. Richter, *ibid.* 1910, 43, 3603; 1911, 44, 3466; 1913, 46, 3434; Schlenk and Knorr, Annalen, 1908, 363, 313; 1909, 368, 271; W. Siegmund, Monatsh. 1908, 29, 1087; J. pr. Chem. 1910, ii. 82, 409; 1911, ii. 83, 553; 1915, [ii.] 92, 342; Staedeler, Annalen, 1849, 69, 308; Urban, Monatsh. 1907, 28, 2399; Wichelhaus, Ber. 1872, 5, 248, 846; 1879, 12, 1500; Willstätter, *ibid.* 1905, 38, 1232; 1906, 39, 3474; 1908, 41, 1458, 3245; 1909, 42, 1909, 4143; Wöhler,

Annalen, 1844, 51, 153; Woskresensky, J. pr. Chem. 1839, i. 18, 419; Zincke and Muhlhausen, Ber. 1905, 38, 756; C. L. Jackson and Bolton, Ber. 1912, 45, 871; J. Amer. Chem. Soc. 1914, 26, 301; Schneider and Meyer, Ber. 1921, 54, 1484; Kremann, Monatsh. 1922, 43, 269; Emmert and Varrenkamp, Ber. 1922, 55, 2322; 1923, 56, 491.

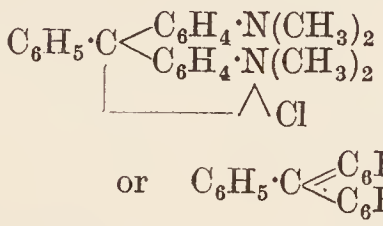
Quinonoïd Compounds.

The term quinones is restricted to substances containing two carbonyl groups; in addition there are a large number of compounds in which the same arrangement of linkages exists, but the oxygen of the carbonyl group is replaced by other atoms or groups. Examples have already been seen in the imines, arylimines, chloroimines, and oximes of the quinones. These compounds have been described in connection with the quinones to which they correspond, as they are generally obtainable directly from the quinones or are converted into them by more or less easy means. In the cases where divalent carbon radicles replace the oxygen of the carbonyl groups there is the same formal relationship, *e.g.*



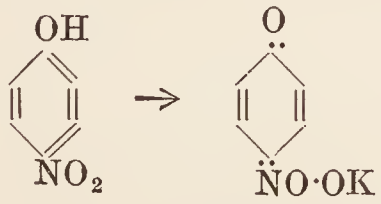
and the 'quinonoïd' structure is evident, but generally such compounds are not directly convertible into the corresponding quinones.

Quinonoïd structure is usually assumed to exist in the case of the organic dyestuffs; thus whether malachite green be written as



or

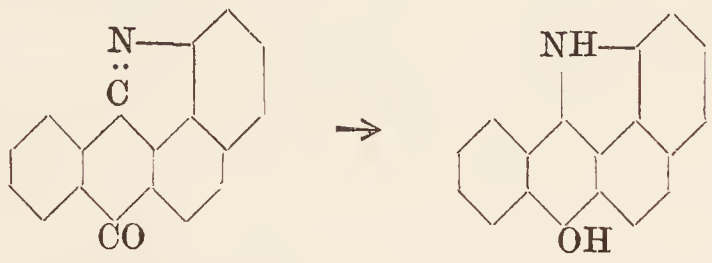
the constitution must be regarded as quinonoïd, the first formula corresponding to the peroxide formula, the second to the diketone formula of *p*-benzoquinone. A discussion of the constitution of dyestuffs is given in the article on Chromophores (*q.v.*), and it is mentioned there that many chemists assume that a rearrangement of linkages takes place when *p*-nitrophenol and allied substances form salts or ionise, the benzenoid giving place to the quinonoïd configuration.



Many quinonoïd compounds exhibit the same additive capacity for hydrogen, hydrogen chloride, &c., as the quinones themselves, and the mechanism of dyestuff formation can frequently be explained by addition to quinonoïd compounds and subsequent oxidation (Bucherer, Ber. 1907, 40, 3412; Green, Chem. Soc. Trans., 1913, 103, 925).

Benzenoid leuco-compounds oxidise spontaneously to the corresponding quinonoïd dyestuffs. It may be noted that marked differences in ease of oxidisability exist, a leuco-compound corresponding to an *o*-quinonoïd dyestuff being far more readily oxidised than one from which a *p*-quinonoïd dyestuff is formed (Green, Chem. Soc. Proc. 1896, 12, 226).

Conversely it is found that quinones vary greatly in their oxidising power. Willstätter and Parnas (Ber. 1907, 40, 1406) show that whereas 2 : 6-(*amphi*-)naphthaquinone shares the strong oxidising properties of *p*-benzoquinone, 1 : 2-(*ortho*-)naphthaquinone shows these on a reduced scale, 1 : 4-(*para*-)naphthaquinone is a feeble oxidising agent, whilst properties of this nature are entirely absent in the case of anthraquinone. Possibly in the last case the explanation is to be found in the fact that the two carbonyl groups link up two real benzene nuclei. Quinonoïd compounds sometimes act as oxidising agents, phenylhydrazine reduces *p*-benzoquinone with evolution of nitrogen at the ordinary temperature; at a higher temperature it reduces aniline black (Willstätter and Cramer, Ber. 1910, 43, 2976), whilst 2 : 9-N-indoloanthrone is reduced by phenylhydrazine at the ordinary temperature (R. Scholl, Ber. 1911, 44, 2370).



The quinonoïd compounds not so far considered are those of such types as

$$>C{:}C_6H_4{:}O \text{ (or :NR and :NR}_2\text{Cl and } >C{:}C_6H_4{:}C<$$

In the first category are many classes of dyestuffs, and reference should be made to the article dealing with triphenylmethane colouring matters. These substances can be considered as derived from quinomethane or its imine

$$CH_2{:}C_6H_4{:}O \qquad CH_2{:}C_6H_4{:}NH$$

by replacement of hydrogen atoms by various groups. To diphenylquinomethane

$$(C_6H_5)_2C{:}C_6H_2{:}O$$

Baeyer has given the name *fuchsone* which lends itself easily to derivatives. Thus pararosaniline becomes diaminodiphenylfuchsonimmonium chloride. The coloured quinonoïd hydrocarbons are derivatives of quinodimethane,

$$CH_2{:}C_6H_4{:}CH_2,$$

and an account of them is given below.

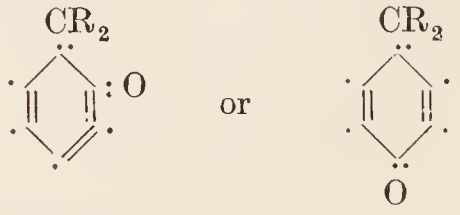
Besides truly quinonoid compounds a number of substances of hemiquinonoid character, possessing the grouping



are known (*e.g.* the pseudoquinols), which also frequently show a tendency to pass into substances of benzenoid configuration.

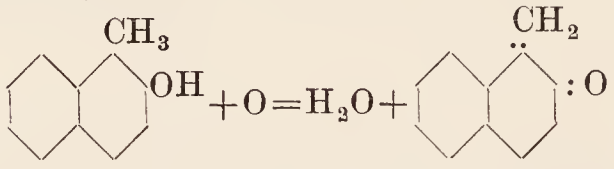
Methylene-quinones or quino-methanes.

These compounds contain the groupings

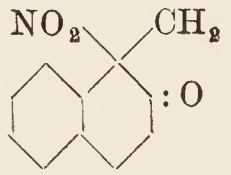


The simplest members of the series, the methylene benzoquinones $CH_2:C_6H_2:O$, are unknown, but many derivatives, substituted either in the methylene group or in the quinonoïd nucleus, have been obtained. Substances of this class have been prepared by the following methods:

1. By oxidation of *o*-methyl substituted naphthols. Fries and Hübner (Ber. 1906, 39, 446) obtained *β*-naphthoquino-1-methane by dissolving 4 grms. of 1-methyl-2-naphthol in 60 c.c. of glacial acetic acid and adding in the course of 1 hour, 12 grms. of sodium nitrite. After 8 hours, the solution was poured into water, the precipitate ground with a little glacial acetic acid, dried on porous earthenware and crystallised from petroleum spirit. Yellow needles, m.p. 132°,



By using nitrous fumes and a solution of the methyl-naphthol in dry ether, a quinitrol



which decomposes and evolves nitric oxide at 140° may be obtained. Derived from this is the *ψ*-quinol $O:C_{10}O_6<^{CH_3}_{OH}$, m.p. 83°. Occasionally the oxidation may be effected by bromine without intermediate formation of a *ψ*:-bromide. Zincke and Walter (Annalen, 1904, 334, 367) obtained benzylidene-2 : 6-dibromoquinone (dibromoquinophenyl methane) by heating bromine with dibromohydroxydiphenylmethane to 100° in carbon tetrachloride solution

$$C_6H_5\cdot CH_2\cdot C_6H_2Br_2OH+Br_2 = 2HBr+C_6H_5\cdot CH:C_6H_2Br_2:O.$$

2. By removing the elements of hydrogen bromide from the *ψ*-bromides formed by the action of bromine on phenols.

$$CH_2Br>^{H}C_6Br_4:O(\text{or } CH_2Br\cdot C_6Br_4\cdot OH)-HBr = CH_2:C_6Br_4:O.$$

The reaction is effected by shaking a benzene solution of the *ψ*-bromide with anhydrous sodium acetate. The tetrabromoquinomethane taken as an example is an amorphous white powder which easily adds hydrogen bromide, water, &c. (Zincke and Böttcher, Annalen, 1905, 343, 100).

3. By dehydration of *p*-hydroxyaryl carbinols

$$(C_6H_5)_2C(OH)(C_6H_4OH) = H_2O+(C_6H_5)_2C:C_6H_4:O,$$

V. Baeyer and Villiger obtained diphenylquinomethane by heating *p*-hydroxytriphenylcarbinol. At 90° only half a molecule of water is eliminated, but a new evolution of water vapour takes place at 150°. The resulting vitreous mass was crystallised from a mixture of ether and benzene; orange needles, m.p. 168° (Ber. 1903, 36, 2792).

4. By heating *p*-methoxytriarylmethyl halides. Bistrzycki and Herbst (Ber. 1903, 36, 2335) obtained diphenylquinomethane by heating anisyldiphenylmethyl chloride for 1 hour at 180°–200°.

$$(C_6H_5)_2CCl(C_6H_4OCH_3) = CH_3Cl+(C_6H_5)_2C:C_6H_4:O$$

Staudinger (Ber. 1908, 41, 1355; *see* also Staudinger and Bereza, Annalen, 1911, 380, 243) finds that ketenes react in the cold with quinones giving *β*-lactones. The latter, when carefully heated below their melting-point, give quinomethanes.

$$(C_6H_5)_2C:C:O+C:C_6H_4:O = (C_6H_5)_2C\overline{\angle CO\cdot O\rangle}C_6H_4:O = CO_2+(C_6H_5)_2C:C_6H_4:O.$$

The corresponding imines are known in some cases. Baeyer, Villiger and Hallensleben (Ber. 1903, 36, 2794) allowed phenylmagnesium bromide to react with *p*-amino-benzophenone, isolated the aminotriphenylcarbinol as picrate, liberated the colourless carbinol base and heated to 160° in a current of hydrogen. The analytical figures obtained for an anhydro-compound, $C_{19}H_{15}N$, are not quite satisfactory. The substance subsequently proved to be a dimeric form (Ber. 1904, 37, 604).

Baeyer and Villiger obtained sharp analytical figures and good results for simple molecular weight with the phenylimine of diphenylquinomethane, $(C_6H_5)_2C:C_6H_4:N\cdot C_6H_5$, m.p. 133°–138°. This red crystalline substance is liberated directly from its salts by the action of alkalis. Treatment with dilute acids gives the corresponding colourless carbinol, whilst stronger acids give the coloured salts of the phenylimine (Baeyer and Villiger, Ber. 1904, 37, 608).

The quinomethanes and their imines are chiefly noted for the ease with which a molecule of water, acid, &c., is added. Thus tetrabromoquinomethane regenerates the *ψ*-bromide with hydrobromic acid, alkalis in acetone solutions give tetrabromohydroxybenzyl alcohol and tetrabromohydroxybenzyl-acetone.

$$CH_2:C_6Br_4:O+H_2O = HO\cdot CH_2\cdot C_6Br_4\cdot OH$$
$$CH_2:C_6Br_4:O+CH_3\cdot CO\cdot CH_3 = CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot C_6Br_2\cdot OH.$$

Diphenylquinomethane (fuchsone) is reduced by zinc and acetic acid to hydroxytriphenylmethane, and on boiling with dilute potash adds the elements of water, giving hydroxytriphenyl carbinol. On the other hand, *p*-trihydroxytriphenyl carbinol is incapable of existence, losing water and passing into dihydroxyfuchsone or pararosolic acid.

Whilst the carbinol bases are colourless, the quinonoid anhydro- bases are coloured, although their shade differs considerably from that of their salts. The following table, due to Willstätter, shows this clearly.

Imine.	Colour of Solution.	Salts.	Reference.
$C(C_6H_5)_2:C_6H_4:N\cdot C_6H_5$	Red		B. & V., Ber. 1904, 37, 597
$C(C_6H_5)(C_6H_4\cdot NH_2):C_6H_4:NH$	Yellow	Döbner's violet	B. & V., Ber. 1904, 37, 2848
$C(C_6H_5)(C_6H_4\cdot NHC_6H_5):C_6H_4:N\cdot C_6H_5$	Brownish-red	Viridine	B. & V., Ber. 1094, 37, 2848
$C(C_7H_6\cdot NH_2)_2:C_7H_6:NH$	Orange-yellow	New fuchsine	W. & P., Ber. 1908, 41, 1458
$C(C_6H_4\cdot NHC_6H_5)_2:C_6H_4:N\cdot C_6H_5$	Red-brown	Aniline blue	B. & V., Ber. 1904, 37, 2848
$C[C_6H_4\cdot N(CH_3)_2]_2:C_1H_6:NC_2H_5$	Orange-yellow	Victoria blue R.	N. & P., Ber. 1908, 41, 579

In the above, B. and V. stands for Baeyer and Villiger, W. and P. for Willstätter and Piccard, and N. and P. for Nölting and Philipp. Besides the references given, the following papers may also be consulted: Auwers, Ber. 1911, 44, 788; Bistrzycki, *ibid.* 1901, 34, 3073; 1903, 36, 3558, 3565; 1912, 45, 1429; Baeyer and Villiger, *ibid.* 1904, 37, 1183, 3191; Annalen, 1907, 354, 152; Zincke, J. pr. Chem. 1898, ii. 58, 441; 59, 228; Annalen, 1903, 329, 1; 1908, 363, 246; Dilthey and Taucher, Ber. 1920, 53, 252; Dilthey and Bloss, J. pr. Chem. 1921, 101, 207; Dilthey and Burger, Ber. 1921, 54, 825.

Quinodimethanes.

The simplest quinonoïd hydrocarbon, quinodimethane or *p*-xylylene



has not been isolated; several derivatives have, however, been prepared. Removal of bromine from diphenyl-*p*-xylylene dibromide,

$$C_6H_5\cdot CHBr\cdot C_6H_4\cdot CHBr\cdot C_6H_5,$$

by means of mercury or silver gives a yellow substance which is probably diphenyl-*p*-xylylene; it is, however, too unstable to isolate (Thiele and Balhorn, Ber. 1904, 37, 1465). Sufficient stability is usually secured by replacing the four hydrogen atoms of the methylene groups by hydrocarbon radicles.

A few compounds of the type $CRR':C_6H_4:CH_2$ have been obtained, *e.g.* where $R = C_6H_5$ and $R' = C_{10}H_7$ or $o\text{-}CH_3\cdot C_6H_4$. These were obtained as blue or violet powders by W. Schlenk and E. Meyer (Ber. 1919, 52, 8), using method (iv.) given below.

Methods of Preparation.

(i.) By removing bromine from substituted *p*-xylylene dibromides. The dimethyl ether of tetraphenyl-*p*-xylylene glycol,

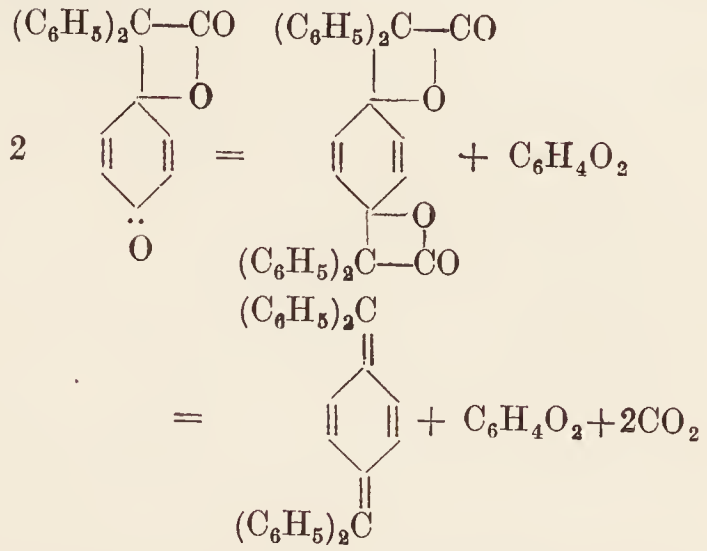
$$(C_6H_5)_2C(OCH_3)\cdot C_6H_4\cdot C(OCH_3)(C_6H_5)_2,$$

is obtained from dimethyl terephthalate by the Grignard reaction and converted into the corresponding dibromide by a solution of hydrogen bromide in glacial acetic acid. The tetraphenyl-*p*-xylylene dibromide is dissolved in 50 times its weight of benzene and boiled in the dark for 20 hours with $1\frac{1}{2}$ times its weight of molecular silver.

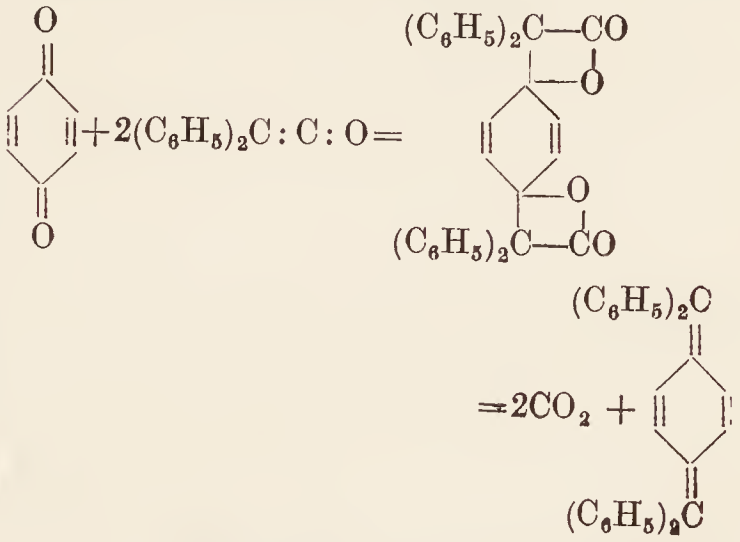
$$(C_6H_5)_2CBr\cdot C_6H_4\cdot CBr(C_6H_5)_2+2Ag = 2AgBr+(C_6H_5)_2C:C_6H_4:C(C_6H_5)_2.$$

The solution is filtered hot and frozen. On allowing the benzene to melt, a residue of the quinonoïd hydrocarbon is left; less pure material is contained in the mother-liquor. The substance is crystallised in absence of light and air from petroleum of b.p. 100°–130° (Thiele and Balhorn, Ber. 1904, 37, 1469).

(ii.) Tetraphenylquinodimethane is formed when the mono-β-lactone obtained from diphenylketene and quinone is heated in a high boiling-point solvent.



(iii.) A better way is to add an excess of diphenylketene to a solution of quinone in petroleum ether. On standing for a day, the di-β-lactone decomposes spontaneously (Staudinger, Ber. 1908, 41, 1355).

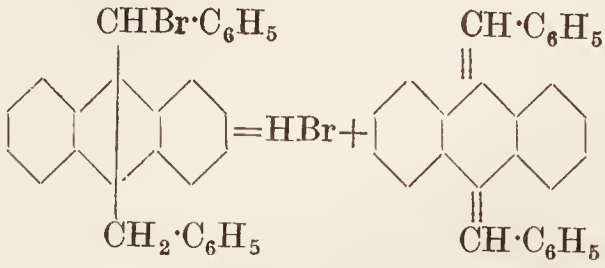


A modified method consists in fusing diphenylketenequinoline with the necessary quinone in an atmosphere of carbon dioxide (Staudinger and Bereza, Annalen, 1911, 380, 243).

(iv.) Hydrogen chloride may be removed from compounds of the type of *p*-benzhydryltriphenylchloromethane on boiling with xylene and quinoline (Tschitschibabin, Ber. 1908, 41, 2770; Schlenk and Meyer, Ber. 1919, 52, 8).

$$(C_6H_5)_2CCl\cdot C_6H_4\cdot CH(C_6H_5)_2+C_9H_7N = C_9H_7N\cdot HCl+(C_6H_5)_2C:C_6H_4:C(C_6H_5)_2.$$

Dibenzaldihydroanthracene is obtained by eliminating hydrogen bromide from bromodibenzylanthracene (Lippmann and Fritsch, Monatsh. 1904, 25, 793).



Tetraphenylquinodimethane forms shining needles of the colour of powdered potassium dichromate; m.p. 239°–242° (Thiele and Balhorn), 240° (Tschitschibabin), 240°–242° (Staudinger). Difficultly soluble in all solvents; the solutions are intensely yellow or orange in colour and show strong gold-coloured fluorescence. The colour of the solutions fades quickly on exposure to light. Bromine is added immediately and iodine liberated from hydrogen iodide in carbon tetrachloride solution. Baeyer supposes the colour of the compound may be explained by the existence of double carbonium linkages (Ber. 1905, 38, 576).

The following similar quinonoid compounds have been obtained.

p-**Bromotetraphenylquinodimethane,** m.p. 257°–259°, Tschitschibabin.

Triphenyl-*p*-tolylquinodimethane, m.p. 197°, Tschitschibabin.

Triphenyl-α-naphthylquinodimethane, m.p. 240°–241°, Tschitschibabin.

Diphenyl-dibiphenylquinodimethane, m.p. above 290°, Schlenk and Brauns, Ber. 1913, 46, 4061.

Tetraphenyltoluquinodimethane, m.p. 200°–210°, Staudinger and Bereza.

Tetraphenylchlorotoluquinodimethane, m.p. 195°–200°, Staudinger and Bereza.

Tetraphenyl - *m* - dichlorotoluquinodimethane, m.p. 225°, Staudinger and Bereza.

Tetraphenyl - *p* - xyloquino - 2 : 5 - dimethane, m.p. 200°, Staudinger.

Tetraphenyl-α-naphthoquinodimethane, m.p. 262°–263°, Staudinger.

Diphenylanthraquinodimethane, m.p. 234°–236°, Lippmann and Fritsch.

Tetraphenyldiphenoquinodimethane

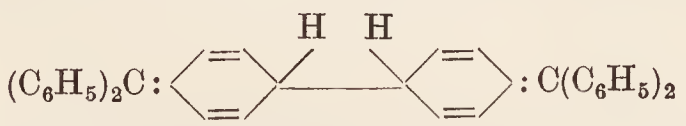
$$(C_6H_5)_2C : C_6H_4 : C_6H_2 : C(C_6H_5)_2.$$

By the action of metals (zinc, silver, copper, &c.) on solutions of the dichloro- compound

$$(C_6H_5)_2CCl{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CCl(C_6H_5)_2.$$

The solution acquires the colour of permanganate. On evaporation of the solvent, the hydrocarbon is left as a violet powder which, in a moist condition, absorbs oxygen rapidly (Tschitschibabin, Ber. 1907, 40, 1818).

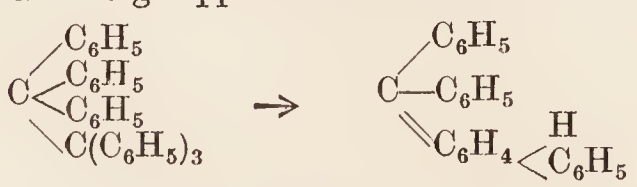
Pyrene, as will be seen from its structure (*v.s.*), must be classed as a quinonoïd hydrocarbon; and quinonoïd formulæ have been suggested for the so-called 'triphenylmethyl' obtained by Gomberg by the action of metals on triphenylmethyl chloride. Heintschel (Ber. 1903, 36, 320, 579) has suggested the structure



whilst Jacobson (*ibid.* 1905, 38, 196) thinks most of the reactions of the substance agree with the formula



Gomberg supposes that the structures



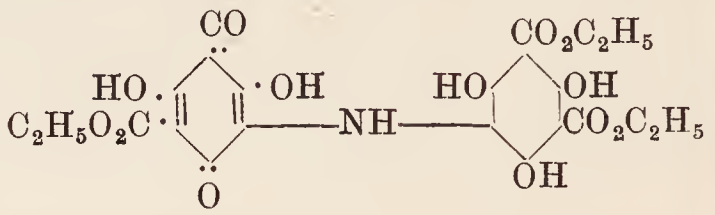
are tautomeric (Ber. 1907, 40, 1881).

Amongst many papers dealing with the structure of 'triphenylmethyl,' the following may be consulted: Tschitschibabin (Ber. 1907, 40, 1810, 3056); Schlenk, Mair and Bornhardt (*ibid.* 1911, 44, 1169); Wieland (Annalen, 1911, 381, 200; Ber. 1911, 44, 2250, 2557). Wieland's discovery that the peroxide of triphenylmethyl gives tetraphenyldiphenoxyethane,

$$(C_6H_5)_2(C_6H_5O)C{\cdot}C(OC_6H_5)(C_6H_5)_2,$$

seems to be important.

The attempts of Staudinger and Clar (Ber. 1911, 44, 1623) to prepare quinoketenes of the types, $O : C : C_6H_4 : C : O$, $(C_6H_5)_2C : C_6H_4 : C : O$, and $O{:}C{:}C_6H_4{:}C{:}C_6H_4{:}C{:}O$, proved unsuccessful: a substance is, however, known to which a quinomonoketene structure, viz.:—

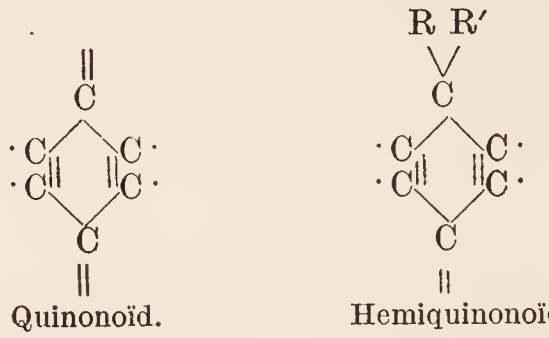


has been ascribed (Leuchs and Theodorescu, Ber. 1910, 43, 1239).

Remarkable hydrocarbons, leucacene, rhodacene and chalcacene, have been found to accompany the acenaphthylene produced from acenaphthene pyrogenetically. They are supposed to contain quinonoid linkages (Podgórska, Lemberger and Suszka, Ber. 1920, 53, 2173).

Hemiquinoïd Compounds.

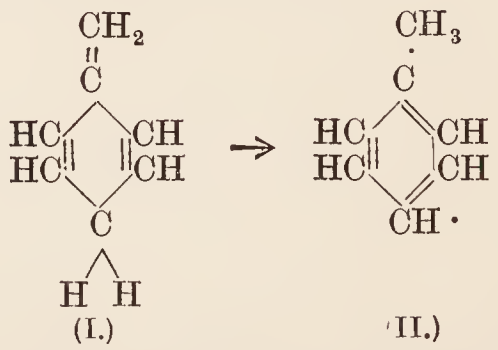
Several compounds already referred to contain a grouping which can be described as hemiquinonoïd. The *cyclo*-hexadiene ring is intact but the carbonyl group (or its equivalent $>C : N—$, $>C : C<$) is only found once, the other carbonyl group being represented by a carbon atom attached to two monovalent radicles



Quinonoïd. Hemiquinonoïd.

Hydrocarbons.

Instead of the term 'hemiquinonoïd,' Auwers refers to compounds of this type as 'semibenzenoïd.' The parent substance of the group would be a hydrocarbon of structure (I.). It is probably incapable of existence, and any reactions devised for obtaining it would result in the production of toluene (II.).



(I.) (II.)

A dimethyl derivative shows sufficient stability for isolation (Auwers and K. Müller, Ber. 1911, 44, 1595).

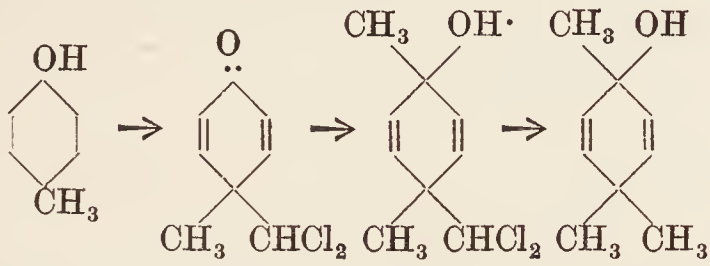
1 : 1-**Dimethyl-4-methylene** *cyclo*- $\Delta^{2,5}$-**hexadiene** C_9H_{12} or



A hemiquinonoïd ketone of the structure



is prepared by the action of chloroform and sodium hydroxide on *p*-cresol (Ber. 1905, 38, 1705). This reacts normally with magnesium methyliodide, yielding a carbinol which need not be isolated before reduction in moist ether-alcohol solution to trimethyl-*cyclo*-hexadiene-ol (colourless needles, m.p. 43°–44°).

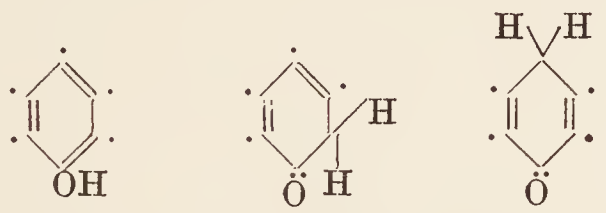


The carbinol loses a molecule of water when shaken for 20 minutes with 10 p.c. sulphuric acid and ice. The resulting 1 : 1-dimethyl-4-methylene-*cyclo*-$\Delta^{2,5}$-hexadiene is extracted with ether, the ethereal extract dried over calcium chloride and distilled under reduced pressure: b.p. 50° at 23 mm.; unstable. The molecular refraction and dispersion are far higher than for the isomeric benzenoïd compounds (mesitylene, pseudo-cumene and methylethylbenzene).

Other papers by Auwers on compounds of 'semibenzene' type may be referred to (Ber. 1903, 36, 1861, 3902; 1905, 38, 1697; 1906, 39, 3748; Annalen, 1907, 352, 219, 273, 288; Ber. 1910, 43, 3094; 1911, 44, 588, 788, 1595, 3679).

PSEUDOPHENOLS.

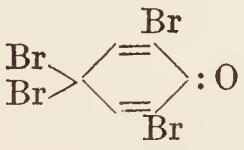
If the idea of keto-enolic tautomerism is extended to the phenols, each hydroxy-derivative of benzene corresponds to two keto*cyclo*-hexadienes



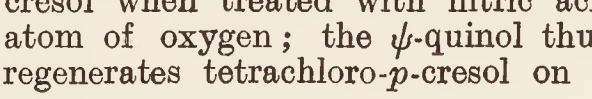
In the case of phenol and its simpler derivatives, the possibility of isolating desmotropic forms appears to be remote, the tribromophenol bromide $C_6H_2OBr_4$, obtained by adding strong bromine water to a solution of phenol in 600–1000 parts of water, and to which Benedikt (Annalen, 1879, 199, 128; Monatsh. 1880, 1, 360) assigned the constitution

$$2{:}4{:}6\text{-}C_6H_2Br_3\cdot OBr;$$

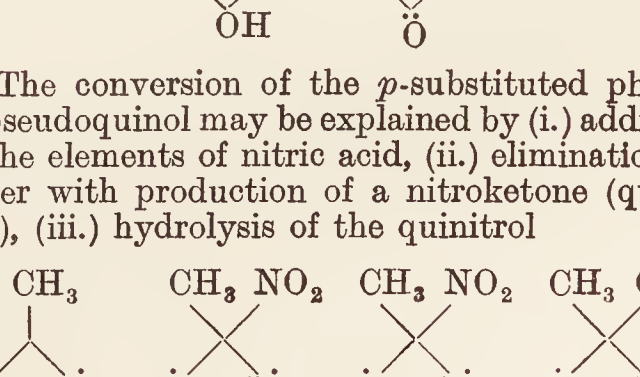
is almost certainly to be formulated as



(Thiele and Eichwede, Ber. 1900, 33, 673), for on digestion with lead acetate in acetic acid, 2 : 6-dibromoquinone is produced. It has been suggested that mineral acids and phenols yield oxonium salts derived from the ketonic form (Chem. Soc. Trans. 1904, 85, 1229); *e.g.*



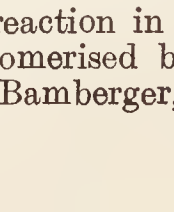
The homologues of phenol when treated with an excess of halogen, yield products insoluble in alkali (Auwers, Ber. 1895, 28, 2888, 2902, 2910; Zincke, *ibid.* 3121). To the 'pseudophenols,' the structure of true phenols (I.) or of the desmotropic ketones (II.)



may be assigned: mere insolubility in alkali is not a sufficient argument to decide in favour of the ketonic structure.

PSEUDOQUINOLS.

In the case of the pseudoquinols ('chinole,' Bamberger), the hemiquinonoïd structure is necessary, the lowest member of these homologues of quinol has the constitution



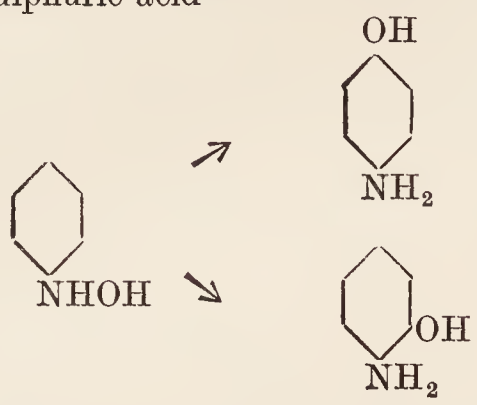
The first monocyclic ψ-quinol was obtained by Zincke (Ber. 1895, 28, 3121), tetrachloro-*p*-cresol when treated with nitric acid adds an atom of oxygen; the ψ-quinol thus produced regenerates tetrachloro-*p*-cresol on reduction.

The conversion of the *p*-substituted phenol to pseudoquinol may be explained by (i.) addition of the elements of nitric acid, (ii.) elimination of water with production of a nitroketone (quinitrol), (iii.) hydrolysis of the quinitrol

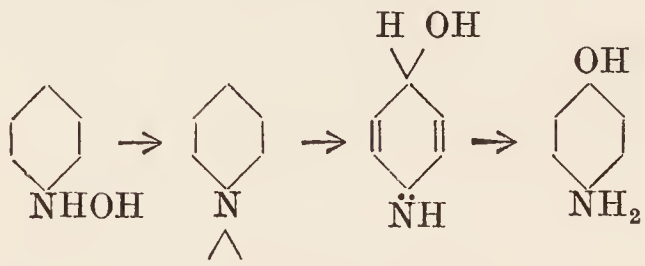
In many cases quinitrols have been isolated.

The discovery of the halogen-free pseudoquinols resulted from experiments (Bamberger, Ber. 1900, 33, 3600) made in order to explain the mechanism of the reaction in which β-phenylhydroxylamine is isomerised by sulphuric acid to *p*-aminophenol (Bamberger, *ibid.* 1894, 27,

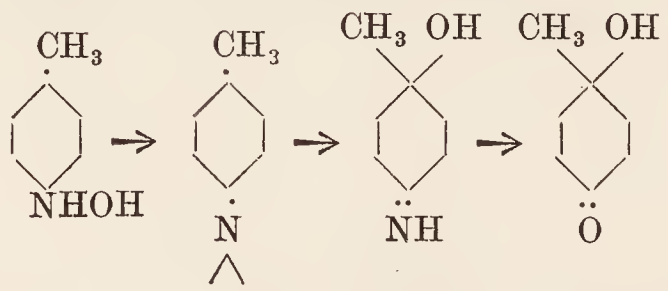
1349, 1552; Wohl, *ibid.* 1434). Similar reactions were observed in cases where the *p*-position to the hydroxylamino-group was unoccupied; with a *p*-halogen atom derivatives of *o*-aminophenol were obtained, and even in the case of hydroxylaminobenzene itself, *o*-aminophenol is produced by the action of alcoholic sulphuric acid



It should be mentioned that with alcoholic sulphuric acid, *p*-phenetidine is formed under certain conditions (Bamberger and Lagutt, Ber. 1898, 31, 1500). Bamberger assumed that in the ordinary reaction the first action of sulphuric acid was to remove the elements of water with production of an 'aryl-imide,' Ar·N<, that this adds water giving an 'imidodienol' which then rearranges itself to a *p*-aminophenol

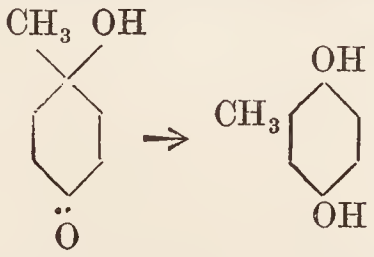


If such a β-arylhydroxylamine be alkyl substituted in the para position to the hydroxylamino-group the last stage is evidently impossible, but the imino- group will be hydrolysed by the acid and a pseudoquinol result

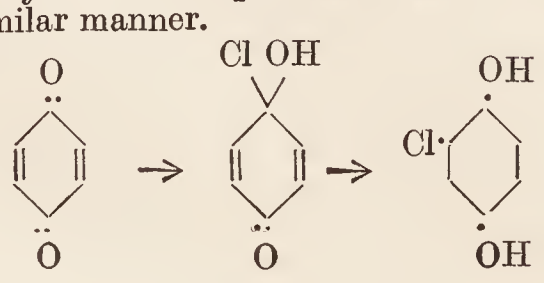


(Bamberger, Ber. 1900, 33, 3600; 1901, 34, 61; 1912, 390, 131; Zincke, *ibid.* 253).

The continued action of dilute sulphuric acid on the pseudoquinol causes isomerisation



The reaction takes place very slowly in the cold, more rapidly on warming. Possibly the action of the hydracids on quinone is to be explained in a similar manner.



Pseudoquinols are also obtained by the action of Grignard's reagents on quinones (Bamberger and Blangey, Ber. 1903, 36, 1625).

Reactions.

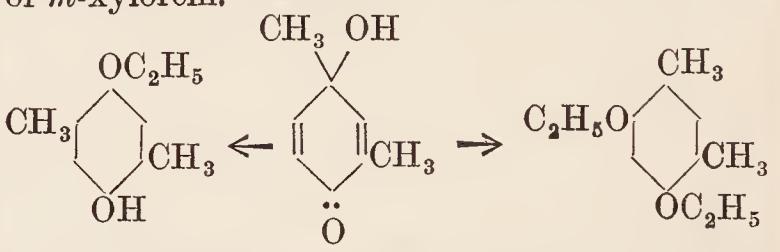
(i.) The hydrazones of the ψ-quinols lose water and give azo- compounds.

$$\begin{matrix}CH_3\\HO\end{matrix}\!>\!C_6H_4:O \rightarrow \begin{matrix}CH_3\\HO\end{matrix}\!>\!C_6H_4:N\cdot NH\cdot R \rightarrow CH_3\cdot C_6H_4\cdot N:N\cdot R$$

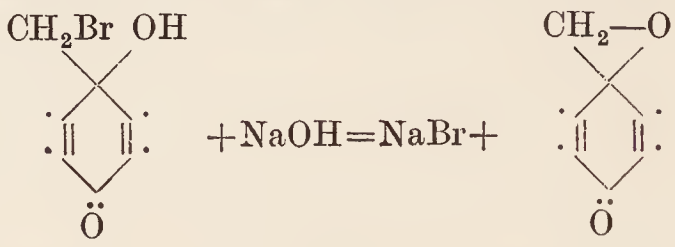
(Bamberger, *ibid.* 1902, 35, 1424).

(ii.) By reduction, phenols are obtained.

(iii.) With alcoholic sulphuric acid, derivatives of quinol and resorcinol are obtained, *e.g.* xylo-ψ-quinol gives a mixture of the monoethyl ether of *p*-xyloquinol and the diethyl ether of *m*-xylorcin.



(iv.) Pseudoquinols with the group CH_2Br lose hydrogen halide on treatment with soda



Methyl-ψ-quinol $\begin{matrix}CH_3\\HO\end{matrix}\!>\!C_6H_4:O$. The product of the transformation of this compound, homoquinol $C_6H_3(CH_3)(OH)_2$, was obtained by the action of dilute sulphuric acid on *p*-hydroxylaminotoluene (Bamberger, Festschrift Zurich, 1896, ii. 179). The ψ-quinol was subsequently isolated, its reactions with hydrazines are described by Bamberger at a later date (Ber. 1902, 35, 1426); m.p. 75°–76° (Annalen, 1912, 390, 165).

Tetrachloro-methyl-ψ-quinol $\begin{matrix}CH_3\\HO\end{matrix}\!>\!C_6Cl_4:O$, by oxidation of tetrachloro-*p*-cresol with warm nitric acid. Gives an *acetyl derivative* (Zincke, Ber. 1895, 28, $3_1$22). Cold nitric acid yields a *nitro ketone* $\begin{matrix}CH_3\\NO_2\end{matrix}\!>\!C_6Cl_4:O$ (Zincke, *ibid.* 1901, 34, 258).

Tribromo-methyl-ψ-quinol $\begin{matrix}CH_3\\HO\end{matrix}\!>\!C_6HBr_3:O$, m.p. 128°, *acetyl derivative*, m.p. 127°–128°.

Tetrabromo-methyl-ψ-quinol $\begin{matrix}CH_3\\HO\end{matrix}\!>\!C_6Br_4:O$, m.p. 205°; *acetyl derivative*, m.p. 175°–176°; *nitro-ketone* $\begin{matrix}CH_3\\NO_2\end{matrix}\!>\!C_6Br_4:O$ (Zincke, Ber, 1901, 34, 258).

2 : 4-**Dimethyl-ψ-quinol** $\begin{matrix}CH_3\\HO\end{matrix}\!>\!C_6H_3(CH_3):O$. By the action of a mixture of 1 part concentrated sulphuric acid and 20 parts of water on 2 parts of *m*-xylylhydroxylamine

$$(NHOH:CH_3:CH_3=1:2\ 4).$$

The mixing is effected at 15°, the reaction continues 8–10 days at 22°–25° in vessels filled

with carbon dioxide. Filter from precipitate, extract the latter with boiling water, add washings to filtrate, acidify the liquid with a mixture of 4 grms. sulphuric acid and 4 grms. of water and extract 50–60 times with ether. Dry the ethereal extract with calcium chloride, distil off the solvent, remove any adhering oil from the residue and recrystallise from a small quantity of boiling water, decolorising with animal charcoal. The *ψ*-quinol separates as a colourless hydrate, $C_8H_{10}O_{21},H_2O$, yield 60 p.c. of the theoretical. Colourless rhombic prisms, m.p. 73°–73·5°. Difficultly soluble in cold, easily in boiling water, readily soluble in organic solvents, petroleum ether excepted. Exhibits weak acid character; the sodium hydroxide solution assumes in succession yellow, brown, and violet-red shades if air be allowed access. In absence of air, alkalis effect isomerisation to *p*-xyloquinol ($CH_3 : CH_3 : OH : OH = 1:4:2:5$), ferric chloride soon produces the smell of xyloquinone. *Benzoyl derivative*

$$\begin{matrix}CH_3\\C_6H_5CO\cdot O\end{matrix}\!>\!C_6H_3(CH_3) : O$$

m.p. 72·5°–73·5° (Bamberger and Brady, Ber. 1900, 33, 3642).

Tribromo- derivative $\begin{matrix}CH_3\\HO\end{matrix}\!>\!C_6Br_3(CH_3) : O$, from *tribromo-m*-xylenol and nitric acid, m.p. 176° (Zincke, Ber. 1901, 34, 258).

Tribromo-ethyl-*ψ*-quinol $\begin{matrix}C_2H_5\\HO\end{matrix}\!>\!C_6HBr_3 : O$, m.p. 105°.

Tetrabromo-ethyl-*ψ*-quinol $\begin{matrix}C_2H_5\\HO\end{matrix}\!>\!C_6Br_4 : O$ (Zincke, *l.c.*).

2 : 4 : 6-**Trimethyl-*ψ*-quinol**

$$\begin{matrix}CH_3\\HO\end{matrix}\!>\!C_6H_2(CH_3)_2 : O.$$

From mesitylhydroxylamine, m.p. 45·5°–46°. *Benzoyl derivative*, m.p. 128·5° (Bamberger and Rising, Ber. 1900, 33, 3636).

Hemiquinonoïd formulæ have been assigned to several classes of compounds. Heintschel's and Jacobson's formulæ for 'triphenylmethyl' are of this type as are also the formulæ proposed by Cain and Morgan for the aromatic diazonium salts.

Papers relating to ψ-quinols, ψ-bromides and quinitrols.

Auwers and co-workers: 1895, Ber. 28, 2888, 2902, 2910; 1896, *ibid.* 29, 1095, 1110, 1120, 1129, 2329, 2348; 1897, *ibid.* 30, 744, 753, 755; 1898, Annalen, 301, 203, 266; 302, 76, 99, 107, 131; Ber. 1899, 32, 2978, 3005, 3016, 3034, 3273, 3281, 3297, 3309, 3317, 3440, 3454, 3466, 3475, 3583, 3587, 3598; 1901, *ibid.* 34, 4256, 4267; 1902, *ibid.* 35, 114, 124, 131, 144, 425, 443, 455, 465, 4207; 1903, *ibid.* 36, 1861, 1878; 1904, Annalen, 334, 264; 1905, Ber. 38, 1693, 3302; 1906, Annalen, 344, 93, 141, 171, 194, 227, 257; Ber. 1922, 55, 2167.

Bamberger and co-workers: 1900, Ber. 33, 3600, 3623, 3636, 3642; 1902, *ibid.* 35, 1424, 3886; 1903, *ibid.* 36, 2028; 1907, *ibid.* 40, 1893, 1906, 1908, 1918, 1932, 1949, 1956; 1913, *ibid.* 46, 787.

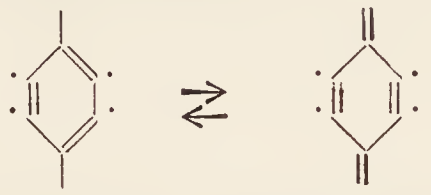
Fries and co-workers: 1906, Ber. 39, 435; 1907, Annalen, 353, 325; 1908, Ber. 41, 2614; 1909, *ibid.* 42, 3375, 3381.

Stephani: Ber. 1901, 34, 4283.

Zincke and co-workers: 1895, Ber. 28, 3121; 1897, J. pr. Chem. ii. 56, 157; 1898, *ibid.* ii. 58, 441; 1900, *ibid.* ii. 61, 561; 1901, *ibid.* ii. 63, 183; 1902, Annalen, 320, 145, 179, 199, 220; 322, 174, 220; 325, 19, 44, 67; 1903, *ibid.* 328, 261; 330, 61; 1904, *ibid.* 335, 157; 1905, *ibid.* 338, 236; 341, 309, 355; 343, 75, 100; 1906, *ibid.* 349, 67, 83, 99, 107; 350, 269; 1907, *ibid.* 353, 357; Ber. 40, 679; 1908, Annalen, 362, 201, 221; 1911, *ibid.* 381, 28; Ber. 44, 176; Annalen, 1912, 388, 294; 394, 3.

Quinonoid Rearrangement.

Under this heading, the linkage changes represented schematically by



will be considered. The rearrangement from benzenoïd to quinonoïd configuration will receive most attention as it is reversible. Reference has already been made to the assumption that coloured organic compounds possess a quinonoïd structure (*v.s.* this article and Colour and Constitution), the first steps in this direction being undoubtedly due to the researches of Otto and Emil Fischer on the dyestuffs of the rosaniline group (Annalen, 1878, 194, 272). Coloured pararosaniline (salt) yields a colourless base on treatment with alkali (A. Rosenstiehl, Ann. Chim. 1876, v. 8, 192), the compound obtained by the action of potassium cyanide is also colourless (H. Müller, Zeitsch. f. Chem. 1866, 2; O. and E. Fischer, Annalen, 1878, 194, 274), and so is the paraleukaniline (as well as its salts with acids) obtained by reduction (Hofmann, Jahresb. 1862, 349; O. and E. Fischer, Annalen, 1878, 194, 268). Paraleukaniline is undoubtedly triaminotriphenylmethane, as proved both by its conversion into and derivation from triphenylmethane; the cyano-derivative is triaminotriphenylacetonitrile, and the colourless pararosaniline base may be assumed to have the corresponding structure of a carbinol (*cf.* Hantzsch and Osswald, Ber. 1900, 33, 278). In the case of salt formation, the base does not simply add one or more equivalents of acid, but water is eliminated at the same time; a property usually found associated with ammonium bases with which the pararosaniline base has nothing in common, since it is practically insoluble in water, soluble in organic solvents, and has not the strong alkaline reaction of an ammonium hydroxide. In many cases the colourless carbinol bases of the triphenylmethane group dissolve in cold dilute acids with very little colouration. This, however, develops on standing or warming. The relations between base and salt can be explained by the following scheme:

$$HOC(C_6H_4\cdot NH_2)_3 \xrightarrow{HCl} HOC\lessdot\begin{matrix}(C_6H_4\cdot NH_2)_2\\C_6H_4\cdot NH_2\cdot HCl\end{matrix}$$

$$\xrightarrow{-H_2O} C\lessdot\begin{matrix}(C_6H_4\cdot NH_2)_2\\C_6H_4\cdot NH_2Cl\end{matrix} \text{ or } C\lessdot\begin{matrix}(C_6H_4\cdot NH_2)_2\\C_6H_4 : NH_2Cl\end{matrix}$$

Both alternative formulæ given to the salt are 'quinonoïd,' the first corresponding to the peroxide formula, the second to the diketone formula of quinone. Corresponding relationships hold between the rosaniline base and the salts derived from it (E. and O. Fischer, Ber. 1880, 13, 2205; Annalen, 1878, 194, 283) and the absorption spectra of base and salts was contrasted by Hartley (Chem. Soc. Trans. 1887, 51, 165).

The discovery of the oxonium salts of dimethyl pyrone by Collie and Tickle (Chem. Soc. Trans. 1899, 75, 711) led Baeyer and Villiger to a study of the basic properties of oxygen and ultimately of the salts of triphenylmethane derivatives (Ber. 1901, 34, 2679, 3612; 1902, 35, 1189, 1201, 1754, 3013; 1903, 36, 2774; 1904, 37, 597, 1183, 2848, 3191; 1905, 38, 569, 1156). Rosenstiehl had regarded pararosaniline as possessing the constitution

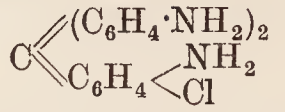
$$(NH_2C_6H_4)_3C—Cl$$

and Baeyer proposed a carbonium structure for the triphenylmethane colouring matters. To represent the substance as a salt in which the halogen is ionisable and is not in ester combination he uses a different symbol, viz.

$$(NH_2C_6H_4)_3C\sim Cl$$

and terms the phenomenon of the production of a coloured salt from a colourless base, *halochromy* (Ber. 1905, 38, 1156). Triphenylcarbinol itself gives coloured salts for which a quinonoïd formula was proposed (Norris and Sanders, Amer. Chem. J. 1901, 25, 54; Kehrmann and Wentzel, Ber. 1901, 34, 3815); to this Baeyer and Villiger objected (Ber. 1902, 35, 1196). The quinonoïd formula was resuscitated by Gomberg (*ibid.* 1907, 40, 1847) but again attacked by Baeyer (*ibid.* 3083). *See also*, Gomberg and West (J. Amer. Chem. Soc. 1912, 34, 1529).

Another 'carbonium' structure, viz.



which is, however, quinonoïd in type, has been suggested by F. Baker (Chem. Soc. Trans. 1907, 91, 1490).

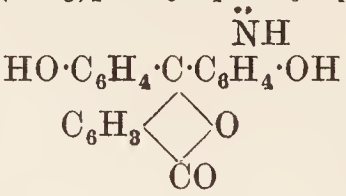
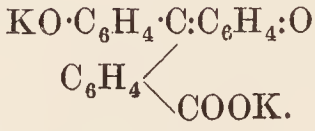
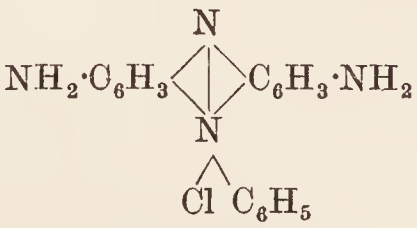
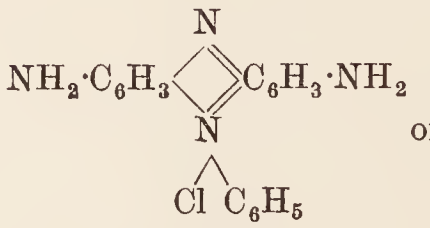
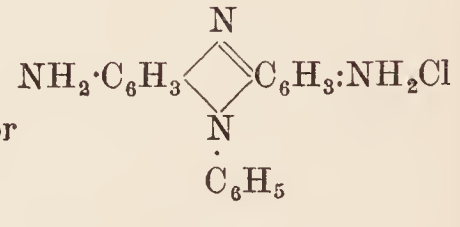
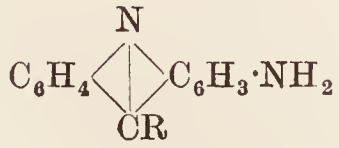
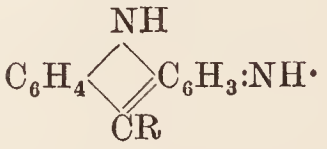
The fact that these dyestuffs are neutral salts is, however, strongly in favour of the halogen being connected with nitrogen rather than carbon, and Baeyer's identification of Homolka's base as diaminofuchsone-imine,

$$C(\cdot C_6H_4\cdot NH_2)_2(:C_6H_4:NH),$$

is favourable to a quinonoïd structure for the salts (Ber. 1904, 37, 2869; 1905, 38, 581; compare H. Weil, *ibid.* 1896, 29, 1541, 2677; 1900, 33, 3141, and v. Georgievics, Monatsh. 1896, 17, 7; 1900, 21, 407; Ber. 1896, 29, 2015). The transient existence of a strongly dissociated ammonium base isomeric with the nearly neutral 'pseudo-base' has been rendered probable in several cases (Hantzsch and Kalb, Ber. 1899, 32, 3109).

That some coloured substances are undoubtedly quinonoïd in structure, and that quinones are themselves coloured, has led to an attempt to represent all coloured organic substances as quinonoïd (*see* especially H. E. Armstrong, Chem. Soc. Proc. 1888, 4, 27; 1892, 8, 101, 103, 143, 189, 194; 1896, 12, 42; Chem. Soc. Trans. 1905, 87, 1272; W. N. Hartley, Chem. Soc. Proc. 1892, 8, 188; Nietzki, Organische Farbstoffe). The subject is very fully discussed by E. R. Watson, Colour in Relation to Chemical Constitution, 1918.

Thus taking some of the more important classes of coloured substances, instead of the formulæ originally assigned to them, quinonoïd formulæ may be substituted. The alternative formulæ of typical compounds are given in parallel columns in the following table:—

Salts of nitrophenols.	$KO\cdot C_6H_4\cdot NO_2$	$O:C_6H_4:NO\cdot OK.$
Salts of nitrosophenols.	$KO\cdot C_6H_4\cdot NO$	$O\cdot C_6H_4:NOK.$
Azophenols.	$C_6H_5\cdot N:N\cdot C_6H_4\cdot OH$	$C_6H_5\cdot NH_2\cdot NH\cdot N:N:C_6H_4:O$
Hydroxy-aldehydes and ketones.	$C_6H_2\cdot CO\cdot C_6H_2(OH)_3$	$C_6H_5\cdot C(OH):C_6H_2(OH)_2:O$
Auramine.	$(CH_3)_2N\cdot C_6H_4\cdot C\cdot C_6H_4\cdot N(CH_3)_2HCl$	$(CH_3)_2N\cdot C_6H_4\cdot C:C_6H_4:N(CH_3)_2Cl.$
Phthaleïns.		
Azines.		 or 
Acridines.		

Reference may be made to the articles dealing with these classes of colouring matters, and the evidence for and against quinonoïd rearrangement taking place on salt formation will alone be considered. The general question of rearrangement of linkages in the molecule on salt formation has been dealt with by Hantzsch (references given under *Nitrophenols*), Decker (many papers, *see* Ber. 1907, 40, 3818; 1908, 41, 3002; Annalen, 1909, 364, 1), Kehrmann (Ber. 1906, 39, 923); Flürscheim (Chem. Soc. Trans. 1910, 97, 84).

The possible quinonoïd structure of diazo-oxides and diazoimides has been suggested

(Bamberger, Ber. 1915, 48, 1354; Morgan, Porter, Upton, Chem. Soc. Trans. 1915, 107, 645; 1917, 111, 187).

Nitrophenols.

In 1892, H. E. Armstrong (Chem. Soc. Proc. 8, 102) expressed the opinion that *o*-nitrophenol, being yellow, really possesses a tautomeric formula $C_6H_4(:NO_2H)(:O)$ and suggested the name *quinoneorthonitroxime*. *p*-Nitrophenol is, however, colourless; the constitution generally assigned to this compound was accepted, but the coloured salts were regarded as quinonoïd. The difference of volatility in a current of steam was adduced as an argument favouring a constitutional difference between the isomers; in the light of more recent work, the non-association of the molecules of the ortho- and the association of those of the para- compound (Auwers, Zeitsch. physikal. Chem. 1893, 12, 689; 1894, 15, 33; 1895, 18, 595, and other papers; Hewitt and Winmill, Chem. Soc. Trans. 1907, 91, 441; Thole, *ibid.* 1910, 97, 2596) may account for the difference in the vapour pressures of the two substances at 100°. Armstrong encountered difficulty with *m*-nitraniline; the compound can hardly be quinonoïd; it is nevertheless coloured, although the benzoate is colourless.

Meanwhile Hantzsch's work on pseudo-acids had appeared and afforded considerable support to the idea that acids and their salts are frequently constituted in a different manner (Ber. 1899, 32, 575, 607, 628, 641, 3066, 3089, 3101, 3137; 1901, 34, 3430; 1902, 35, 210, 226, 265, 1001, 2724; 1905, 38, 1005, 1013, 1022, 2266, 2326; 1906, 39, 139, 162, 1073, 1084, 1105, 2098, 2472, 2478, 2703, 3072, 3080, 4153; 1907, 40, 330, 1523, 1533, 1556, 4875; 1908, 41, 1745; 1909, 42, 966, 986, 1000, 1007; 1910, 43, 45, 68, 82, 95, 1685; 1911, 44, 1783; 1912, 45, 85). In the case of nitroform and its potassium salt, a good case was made out for the respective formulæ (Hantzsch and Rinkenberger, Ber. 1899, 32, 628) $CH(NO_2)_3$ and

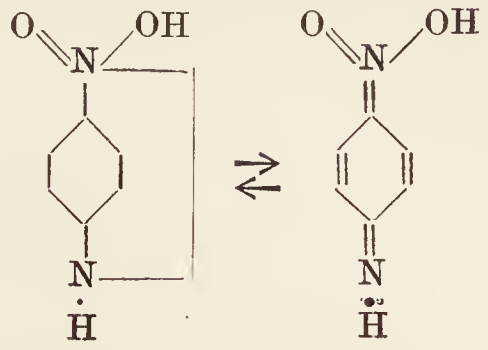
$$C(NO_2)_2(:NO\cdot OK)$$

Hantzsch went so far as to state that any colourless hydrogen compound which gives coloured ions is a pseudo-acid; *i.e.* the free hydrogen compound and its salts possess different constitutions (Ber. 1899, 32, 578).

Other observers have explained anomalous results in the selective absorption or fluorescence of nitro-compounds by assuming the change

$$X(\cdot NO_2)(\cdot OH) \rightarrow X(:NO\cdot OK)(:O)$$

(Chem. Soc. Trans. 1900, 77, 1324; 1902, 81, 893; 1906, 89, 19), whilst Baly, Edwards and Stewart (Chem. Soc. Trans. 1906, 89, 514) concluded from a comparison of the absorption spectra of *p*-nitrophenol and its sodium salt that 'the residual affinity of the oxygen atoms of the nitro-group exerts insufficient attraction for the hydrogen of the free nitrophenol to cause the formation of the quinonoïd form, but that when the hydrogen is replaced by the more electro-positive sodium atom, then the attraction of the oxygen atom is sufficient to bring the sodium over, with the formation of the quinonoïd form.' A similar relationship was assumed in the case of orthonitrophenol and its sodium salt, whilst the yellow colour of *p*-nitroaniline was explained by its molecules existing in quinonoïd phases



The transitory existence of a meta-quinonoïd linking was also assumed to account for the phenomena observed with *m*-nitroaniline and *m*-nitrophenol. Baly and Tuck subsequently extended their views (Chem. Soc. Trans. 1906, 89, 982), stating that the phenylhydrazones of the three nitrobenzaldehydes exist partly or entirely in the quinonoïd form

$$HO\!\!>\!\!O\!\!=\!\!N : C_6H_4 : C : N\cdot NH\cdot C_6H_5$$

whilst *p*-nitrophenylhydrazine and its acetone derivative also exist in the quinonoïd forms

$$HO\!\!>\!\!O\!\!=\!\!N : C_6H_4 : N\cdot NH_2$$

and $$HO\!\!>\!\!O\!\!=\!\!N : C_6H_4 : N\cdot N : C(CH_3)_2$$

A number of *o*-, *m*-, and *p*-nitrophenylhydrazones have been examined with respect to the formation of metallic salts by R. Ciusa (Atti R. Accad. Lincei, 1919, [v.] 28, ii. 366).

Chemical evidence for the assumed change was lacking until Hantzsch and Gorke (Ber. 1906, 39, 1073) showed that under certain conditions the silver salts of the nitro-phenols yield coloured *aci*-esters on reacting with alkyl halides. These compounds are extremely labile, are readily hydrolysed and undergo spontaneous change into the nearly or quite colourless nitro-aryl-alkyl ethers. Hantzsch states that their colour points to quinoïd structure: certainly the ease with which they are hydrolysed is very distinct evidence in favour of the grouping: NO·O Alkyl; in this case the constitution of the methyl derivative of *o*-nitrophenol must be represented by the structure

$$O : C_6H_4 : NO\cdot OCH_3 \text{ or } \overline{O\cdot C_6H_4\cdot NO\cdot OCH_3}$$

As this compound is deep red and the isomeric *o*-nitroanisole practically colourless, grounds exist for assigning the structure

$$O : C_6H_4 : NO\cdot OK$$

to the red potassium salt of *o*-nitrophenol. Similar observations were made with regard to the *aci*-ethyl ethers of 2 : 4- and 3 : 4-dinitrophenols and of 2 : 4 : 6-trinitrophenol. Hantzsch (Ber. 1906, 39, 1102) draws attention to the small affinity constant of 2 : 4 : 6-trichlorophenol ($2{\cdot}8\times10^{-8}$, Walker, Zeitsch. physikal. Chem. 1900, 32, 137) in comparison with trinitrophenol (0·0164, Rothmund and Druker, *ibid.* 1903, 46, 827) which points to dissimilar structures for the negative ions. Comparison of the light absorption and electric conductivity of solutions of nitrophenols points generally to a very low

concentration of the second term in the equilibrium equation

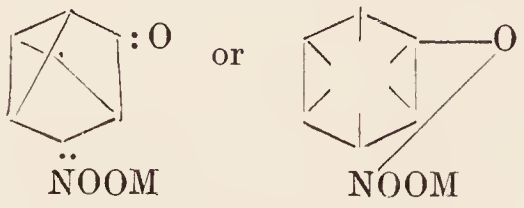
$$X(\cdot NO_2)(\cdot OH) \rightleftharpoons X(:NO_2H)(:O) \rightleftharpoons X(:O)(:NO_2\cdot)'+H'$$

i.e. the *aci-* forms of 2 : 4-dinitrophenol and 2 : 4 : 6-trinitrophenol undergo practically complete dissociation ; possibly in the case of *o*-nitrophenol a measurable amount of non-ionised *aci-* form exists in aqueous solution.

Hantzsch (Ber. 1906, 39, 3080) has developed similar views with regard to the hydroxy-aldehydes and hydroxy-ketones. Many cases exist in which colourless compounds of these types give coloured salts. Hantzsch assumes that the phenolic compounds give rise to quinonoïd salts, *e.g.* in the case of salicylaldehyde and its potassium salt, the following formulæ are adopted

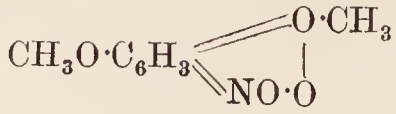
$$C_6H_4\!<\!\begin{matrix}OH\\CHO\end{matrix} \qquad C_6H_4\!<\!\!=\!\begin{matrix}O\\CH\cdot OK\end{matrix}$$

Whilst no inherent difficulty presents itself in accepting quinonoïd formulæ for the coloured alkaline salts of *o-* and *p*-nitrophenols, the fact that *m*-nitrophenol also gives rise to coloured salts must be taken into account. Hantzsch (Ber. 1906, 39, 1095 ; 1907, 40, 330) assigns such formulæ as



to the salts, although *m*-quinones have not so far been isolated. Some interest attaches to substituted phenols such as the 2 : 4-dinitro- and 2 : 4 : 6-trinitro-derivatives. The salts and ions may be of either *o-* or *p*-quinonoïd type. Hantzsch considers the *p*-type is usually preferred : comparisons of the absorption spectra of alkaline solutions of these compounds with the salts of *o-* and *p*-mononitrophenols supports this view (Buttle and Hewitt, Chem. Soc. Trans. 1909, 95, 1755 ; Meldola and Hewitt, *ibid.* 1913, 103, 876). In some cases, two isomeric salts can be obtained. Rabe (Zeitsch. physikal. Chem. 1901, 38, 175) has described yellow and red thallium picrates. These observations have been further extended by Hantzsch, who suggests stereoisomerism as a possible explanation (Ber. 1907, 40, 330).

H. Kauffmann (Zusammenhang zwischen Farbe und Constitution, Ahren's Sammlung, 1904, Enke, Stuttgart) has strongly objected to the hypothesis of a quinonoïd transformation, the alteration from practically colourless nitrobenzene to coloured metallic nitrophenolate being attributed to the auxochromic action of the metaloxyl group. Kauffmann has drawn particular attention to the yellow colour of the dimethyl ether of nitroquinol which, he considers, cannot be other than $C_6H_3(OCH_3)_2NO_2$, hence a certain amount of auxochromic influence must be attributed to the methoxyl group whilst quinonoïd transformation is, in this case, excluded (Ber. 1906, 39, 1959, 2722, 4237 ; 1907, 40, 843, 2338, 2341, 2352 ; 1908, 41, 4396, 4413, 4422 ; 1910, 43, 1214 ; compare Hantzsch, Ber. 1907, 40, 1556, 1572, 3536 ; 1908, 41, 1216). The possibility of nitroquinol dimethyl ether possessing the structure of an internal oxonium salt



should not be entirely disregarded when one bears in mind the strongly basic character of oxygen in quinonoïd compounds containing more than one methoxy group.

Whilst Baly in his earlier papers (*v.s.*) attributed the difference between the absorption spectra of the nitrophenols and their salts to a radical change in constitution, he has subsequently abandoned this view (Baly, Tuck and Marsden, Chem. Soc. Trans. 1910, 97, 571). It is stated that (*l.c.* 588) ' the shape of the absorption curve of quinone and those of the nitro-compounds is quite different. It therefore seems in the highest degree improbable that the shift in the absorption bands, which takes place without any change in type when the nitrophenols are converted into their sodium salts, is due to a radical change of structure, as is demanded by the quinonoïd hypothesis.'

Whether quinone and its ' nitroxime ' (*i.e.* *aci-p*-nitrophenol) would exhibit curves of the same type is unknown. It would certainly be interesting in this connection to determine the absorption spectrum of the quinonoïd salts $C_6H_4(:NOOM)_2$ obtained by partial reduction of *o-* and *p*-dinitrobenzenes (Meisenheimer, Ber. 1903, 36, 4174 ; Meisenheimer and Patzig, *ibid.* 1906, 39, 2526). The constitution of such salts can hardly be other than quinonoïd.

Hantzsch's discovery of a second series of deeply coloured easily hydrolysable alkyl derivatives of the nitrophenols certainly points to a constitution of nitrophenolate ions differing from that of the nitrophenols, and it is difficult to see why an ion $NO_2X\cdot O'$ should be far more negative in character than $Cl\cdot X\cdot O'$ when one compares the ions, NO_2' and Cl', themselves. Moreover, the NO_2 group has different chemical properties when it is attached to radicles such as C_6H_5, $\cdot C_6H_4\cdot OCH_3$, &c., and when it is present in a sodium nitrophenolate. In the former case, warming with sodium methoxide solution yields an azoxy- compound with ease ; in the latter case the transformation seems impossible. On the other hand, the nitrophenols in ammoniacal solution are reduced to aminophenols with great readiness in the cold. Even if the mechanism of these reduction processes is not fully understood, the different course of the reaction with compounds of the two classes (nitro- compounds and salts of nitro-phenols) points to a difference in chemical constitution.

Another case of a nitro- compound furnishing intensely coloured salts is afforded by hexanitrodiphenylamine, the ammonium salt of which was at one time employed as a dyestuff under the name of ' aurantia.' The probability of the salts having a quinonoïd structure is increased by the isolation of a violet *aci*-ether (Hantzsch and Opolski, Ber. 1908, 41, 1745) ; whilst further examples might be quoted in which the possibility of quinonoïd rearrangement of nitro-compounds has been suggested (*see* Meldola, Chem. Soc. Trans. 1911, 99, 1286, 2035 ; Dreaper, *ibid.* 2094).

Some caution is, however, necessary, as

several cases have been observed in which halogen derivatives of phenol give two series of salts, one coloured, the other colourless (Torrey and Hunter, Ber. 1907, 40, 4322; J. Amer. Chem. Soc. 1911, 33, 194; Hantzsch and Scholtze, Ber. 1907, 40, 4875. See further papers on *Chromoisomerism*, Hantzsch, *ibid.* 1910, 43, 1662, 2001, 2572; Biilmann, *ibid.* 1910, 43, 1651; Lucas and Kemp, J. Amer. Chem. Soc. 1921, 43, 1654). It may be noted that metallic salts of primary and secondary nitroamines may be obtained in the ortho- and para- series by adding sodium or potassium ethoxide to hot benzene solutions of nitroanilines (Green and Rowe, Chem. Soc. Trans. 1913, 103, 508. *See* also Cain, Macbeth and Stewart, *ibid.* 586).

Azo- Compounds.

Considerable discussion has arisen with regard to the hydroxyazo- compounds, but the aminoazo- compounds have not received the same amount of attention. The *p*-hydroxyazo- compounds are undoubtedly phenolic in character; the acyl and aryl derivatives have their substituent groups attached to oxygen and not to nitrogen. Dilute nitric acid and bromine give derivatives which from the positions assumed by the nitro- groups or bromine atoms point directly to the phenolic constitution of the original azo- compounds (Hewitt and coworkers, Chem. Soc. Trans. 1900, 77, 99, 712, 810; 1901, 79, 49, 155, 160, 1090; Auwers and Mann, Ber. 1900, 33, 1312). On the other hand, Michler's hydrol behaves towards benzene azo-α-naphthol as it does towards quinonoïd compounds. Physico-chemical examination of the *p*-hydroxyazo- compounds also points to a phenolic formula. We may cite the association observed in hydrocarbon solvents (Auwers and Orton, Zeitsch. physikal. Chem. 1896, 21, 355; Auwers and Mann, Ber. 1900, 33, 1308), and the close similarity of the absorption spectra of the azo-phenols and their alkyl ethers (Tuck, Chem. Soc. Trans. 1907, 91, 449). The *o*-hydroxyazo- compounds generally exhibit similar behaviour. Discussion has arisen with regard to the spectroscopic evidence, Tuck considering that this favours a quinone-hydrazone structure (*l.c.* 453), whereas Auwers draws an opposite conclusion from Tuck's spectrographic measurements (Annalen, 1908, 360, 11; *cf.* Auwers, Ber. 1907, 40, 2154; Annalen, 1911, 381, 265; Charrier and Ferreri, Gazzetta, 1912, 42, ii. 811).

Whilst the metal, alkyl and aryl- derivatives of *p*-hydroxyazo- compounds are derived from the phenolic form, the salts formed with mineral acids in which the azophenols function as bases (Typke, Ber. 1877, 10, 1581; Liebermann, *ibid.* 1883, 16, 2858; Zincke and Bindewald, *ibid.* 1884, 17, 3028; Spiegel, *ibid.* 1885, 18, 1480; Lagodzinski and Matcscu, *ibid.* 1894, 27, 961; dissertations of various Heidelberg students of P. Jacobson: W. Fischer, 1892; F. Marsden, 1892; J. Klein, 1892; F. Düsterbehn, 1893; C. Schwarz, 1893; B. Piepenbrink, 1895; Hewitt and Pope, Ber. 1897, 30, 1624) behave towards substituting agents as if they were derivatives of quinone-hydrazones (Hewitt and co-workers, *l.c.*; Hantzsch, Ber. 1909, 42, 2129; Fox, Chem. Soc. Trans. 1910, 97, 1337). Moreover, these salts, when hydrolysed with water, frequently yield compounds having the composition of one or two molecules of the azophenols united with one molecule of water (Hewitt, Ber. 1895, 28, 799; Hewitt and Pope, *ibid.* 1897, 30, 1624; Farmer and Hantzsch, *ibid.* 1899, 32, 3089; Hantszch and Robertson, *ibid.* 1910, 43, 106). These hydrated compounds [1] differ markedly in colour from the azophenols into which they spontaneously pass on dehydration. If the hydrates be considered as the pseudo-bases corresponding to the salts with mineral acids, their close relationship to the quinone-hydrazones is rendered evident. For the salts themselves, ammonium, oxonium, and carbonium structures have been suggested, *e.g.*

$C_6H_5\cdot NH(HCl)\cdot N : C_6H_5 : O$	Hewitt, Chem. Soc. Trans. 1900, 77, 99.
$C_6H_5\cdot NH\cdot N : C_6H_4 : O<^{H}_{Cl}$	Fox and Hewitt, *ibid.* 1908, 93, 333; and Hantzsch, Ber. 1909, **42**, 2134.
$C_6H_5\cdot NH\cdot N : C_6H_4<^{OH}_{Cl}$ or $^{H}_{Cl}>C_6H_4 : N\cdot NH\cdot C_6H_4\cdot OH$	F. Baker, Chem. Soc. Trans. 1907, 91, 1490.

The ammonium formula is negatived by the practical identity of the absorption spectra of the azophenols and their alkyl ethers in mineral acids, *i.e.* the salts are of similar type. Reasons may be given for preferring the oxonium to the carbonium formula (Fox and Hewitt, *l.c.*).

The relationships existing between benzeneazophenol and its derivatives may be exhibited by the scheme on p. 602, in which M=metal, X=Cl, SO_4H, &c., R=alkyl.

If the evidence given be accepted, it will be seen that alkalis favour a phenolic, acids a quinonoïd structure. The salts of the aminoazo- compounds, *e.g.* $C_6H_5\cdot N : N\cdot C_6H_4\cdot NH_2$, probably possess a quinonoïd structure

$$C_6H_5\cdot NH\cdot N : C_6H_4 : NH_2Cl$$

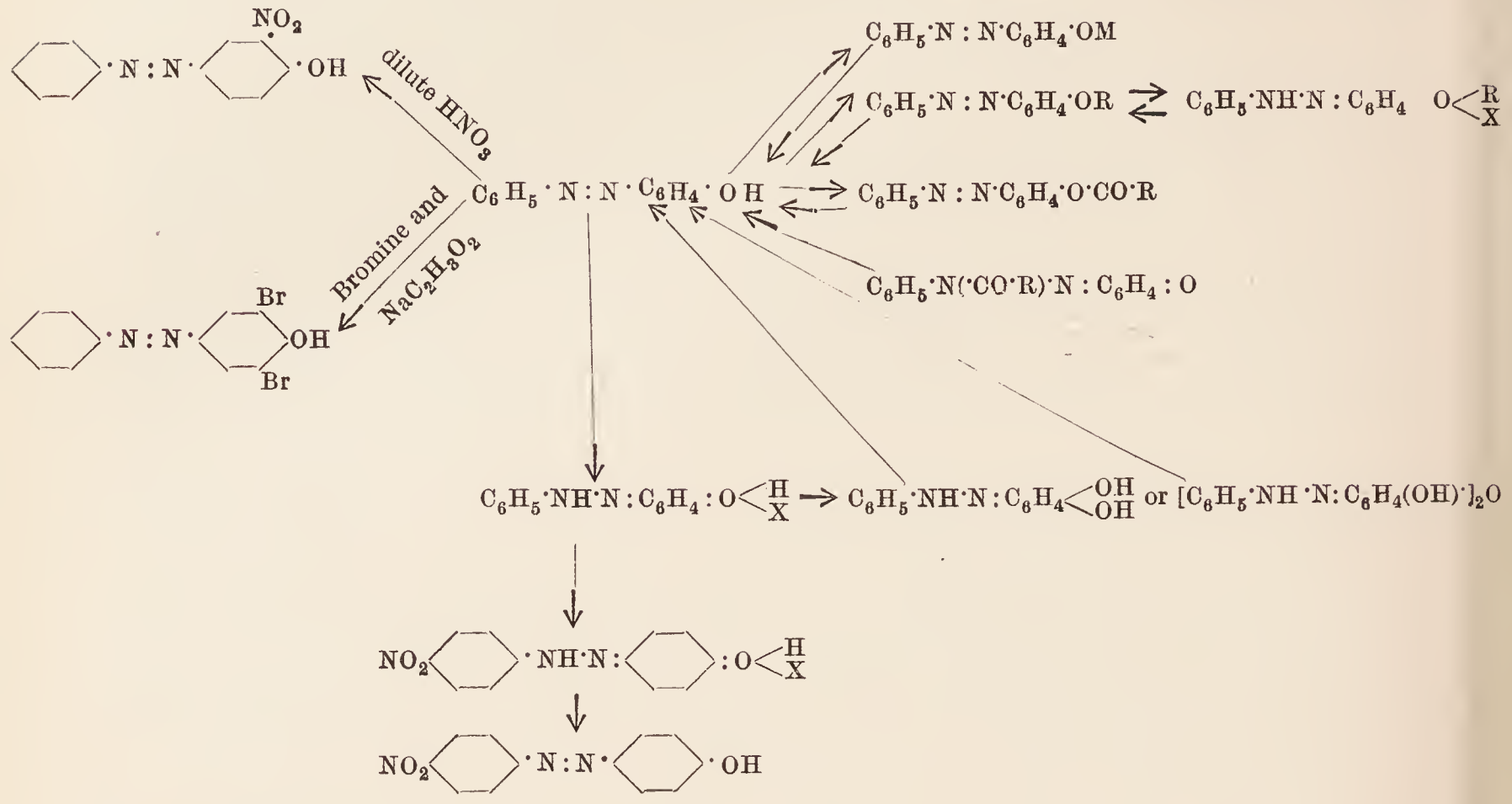
(Hewitt, Analyst, 1908, 33, 85; Ber. 1908, 41, 1986; Hantzsch, Ber. 1908, 41, 1171, 1187, 2435; 1909, 42, 2129; Fox, *ibid.* 1908, 41, 1989; Chem. Soc. Trans. 1910, 97, 1337). Kehrmann and Hempel (Ber. 1917, 50, 856) disagree with this view.

The question of the constitution of the free hydroxyazo- compounds has again been raised, attempts being made to settle the question by electric conductivity determinations (Puxeddu and Gennari, Gazz. chim. ital. 1921, 51, i. 147, 256; 1922, 52, i. 216, 235).

Whilst the simpler hydroxyazo- compounds and their alkaline salts usually give solutions of yellow or brown colour, the *p*-nitro-arylazophenols, though giving brown solutions in neutral solvents, yield alkaline salts which vary from deep red (*p*-nitrobenzeneazophenol) to violet (*p*-nitrobenzeneazo-α-naphthol) or even pure blue. It has been suggested that this difference may be accounted for by supposing the salts to be derivatives of azo-quinones, *e.g.*

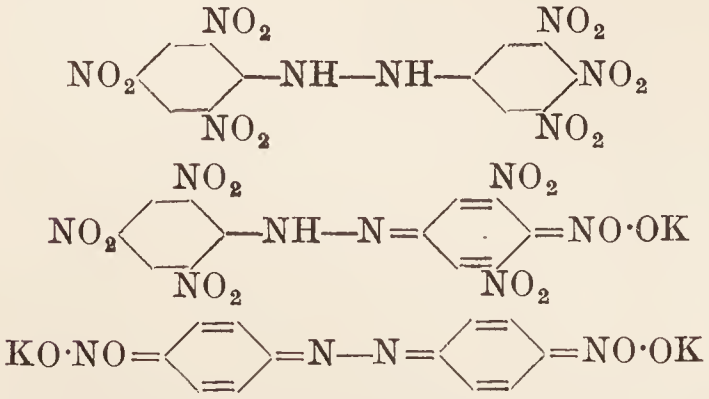
[1] The hydrates were at first mistaken for isomers (Hewitt, Ber. 1893, 26, 2975). Jacobson obtained a modification of *o*-toluene azophenol melting at about 70° (Annalen, 1895, 287, 161); this proved subsequently to be a hydrate (Ber. 1897, 30, 1628).

$KO\cdot NO : C_6H_4 : N\cdot N : C_6H_4 : O$ (Hewitt and Mitchell. Chem. Soc. Trans. 1907, 91, 1251), though this view has been attacked by Baly, Tuck and Marsden (*ibid.* 1910, 97, 1494).



Whereas most azo- compounds readily undergo fission on alkaline reduction (ammonium sulphide) at the double linkage between the nitrogen atoms, such double linkage appears to be absent in the case of the alkaline *p*-nitrobenzeneazophenolates, which are easily reduced to *p*-aminobenzeneazophenol (Meldola, Chem. Soc. Trans. 1885, 47, 659).

Derivatives of hydrazobenzene nitrated in the para- position to the hydrazo- group dissolve in excess of alkali with blue colour. The pale yellow hexanitrohydrazobenzene (m.p. 201°–202°) prepared from hydrazine hydrate and picryl chloride gives both mono- and di-potassium salts; solutions of the first are deep red, of the second, deep blue to blue violet in colour (Grandmougin and Leeman, Ber. 1906, 39, 4384; 1908, 41, 1295). The relationships of the compounds may be represented by the formulæ



Compare Hewitt and Mitchell (Chem. Soc. Trans. 1907, 91, 1254); Raschig (Zeitsch. angew. Chem. 1907, 20, 2040); Hantzsch and Lister (Ber. 1910, 43, 1685).

Similar formation of blue alkaline solution in the case of 4 : 4′-dinitrohydrazobenzene (Lermontoff, Ber. 1872, 5, 232; Janovsky, Monatsh. 1885, 6, 160; Willgerodt, J. pr. Chem. 1890, [ii.] 42, 51; Werner and Stiasny, Ber. 1899, 32, 3272) has been frequently observed. Freundler and Beranger considered the product obtained by the reduction of di-*p*-nitroazobenzene to have a quinonoïd formula (Compt. rend. 1902, 134, 1219). Green and his co-workers bring forward evidence in favour of the substance being truly dinitrohydrazobenzene, the salts, however, being quinonoïd in structure (Chem. Soc. Trans. 1911, 99, 1960; 1912, 101, 2443).

Possibly the deep coloration given when solutions of *p*-nitrophenylhydrazones (Hyde, Ber. 1899, 32, 1810) are made alkaline may be attributed to quinonoïd transformation (compare Baly and Tuck, Chem. Soc. Trans. 1906, 89, 982; Hewitt, Johnson and Pope, *ibid.* 1914, 105, 364). Two modifications of benzaldehyde *p*-nitrophenylhydrazone have been observed: this also holds in the case of the *p*-nitrophenylhydrazones of the nitrobenzaldehydes (Ciusa and Vecchiotti, Atti R. Accad. Lincei, 1911, [v.] 20, i. 803; Ciusa, *ibid.* 1919, [v.] 28, ii. 366; 1920, [v.] 29, ii. 42, 146).

Hydroxyaldehydes and Hydroxyketones.

As mentioned previously, hydroxyaldehydes and hydroxyketones in which the hydroxyl and carbonyl groups stand in the ortho- or para- position to one another, may form salts of quinonoïd type (Hantzsch, Ber. 1906, 39, 3080). The azo- derivatives of salicyl aldehydes have been examined in this repsect by Hewitt and Mitchell (Chem. Soc. Trans. 1907, 91, 1262); Pope and Willett, *ibid.* 1913, 103, 1258; Hewitt, Mann and Pope, *ibid.* 1914, 105, 2193; Sirkar, *ibid.* 1917, 109, 757).

Schiff's bases prepared from hydroxyaldehydes occasionally occur in isomeric modifications. The isomerism is supposed by Manchot to be of phenol-quinone type (Annalen, 1912, 388, 103).

Auramines.

The salts of auramine bases may have a quinonoïd structure. The bases themselves cannot well have other than a ketone-imide constitution and are readily hydrolysed; the salts show greater stability. The possibility that the hydrochloride of ordinary auramine has the constitution

$$(CH_3)_2N\cdot C_6H_4\cdot C(NH_2):C_6H_4:N(CH_3)_2Cl$$

is supported by the existence of a methyl phenyl auramine (D. R. P. 44077) as well as by the work of A. Stock (J. pr. Chem. 1893, ii. 47, 401), which proved that the twice substituted auramines yield ketone and secondary amine on hydrolysis. Graebe (Ber. 1899, 32, 1678) has urged against this view that whilst auramine hydrochloride is easily converted into phenyl auramine by heating with aniline, it is not attacked by methylaniline. Hantzsch and Osswald (Ber. 1900, 33, 278) hold the view that the true auramine base yields a pseudo-base which loses water, giving the imine

$$(CH_3)_2N\cdot C_6H_4\cdot C(NH_2):C_6H_4:N(CH_3)_2OH$$
$$\rightarrow (CH_3)_2N\cdot C_6H_4\cdot C(NH_2)(OH)\cdot C_6H_4\cdot N(CH_3)_2$$
$$\rightarrow (CH_3)_2N\cdot C_6H_4\cdot C(:NH)\cdot C_6H_4\cdot N(CH_3)_2$$

whilst Stock (Ber. 1900, 33, 318) further supports his view by observations on phenylmethyl-auramine cyanide which exists in two forms, a pale yellow of benzenoïd and a yellowish-red of quinonoïd constitution.

Graebe (Ber. 1902, 35, 2615) still urges against the quinonoïd structure of the auramine salts the close resemblance which exists between them and the salts of phenyliminobenzophenone. Graebe's imino-structure has been accepted by L. Semper (Annalen, 1911, 381, 234) who finds that the pale yellow acylated auramine bases yield deep bluish-violet or bluish-green salts with acid. A quinonoïd formula is assigned to the acylated salts, *e.g.*

$$(CH_3)_2N\cdot C_6H_4\cdot C(\cdot NHCOCH_3):C_6H_4:N(CH_3)_2Cl$$

but denied to the salts of auramine, methyl-auramine and phenylauramine on account of the great colour difference.

Phthaleïns.

Phenolphthaleïn and its alkaline salts may well possess different structures in the sense represented by the formulæ already given; corresponding formulæ may be applied in the case of fluoresceïn and the rhodamines. The tautomerism of fluoresceïn has been demonstrated by Nietzki and Schroeter (Ber. 1895, 28, 44) who obtained a mixture of a colourless lactonoïd diethyl-ether and a yellowish-red quinonoïd ether-ester by the direct alkylation of alkali salts of fluoresceïn.

Direct evidence of this character was wanting in the case of phenolphthaleïn until comparatively recently, the supposed oxime of phenolphthaleïn prepared by Friedländer (Ber. 1893, 26, 172, 2258) not possessing the constitution originally assigned to it. The ethers obtained from phenolphthaleïn were colourless and undoubted derivatives of diphenylphthalide. A. G. Green (in part with P. E. King) has demonstrated that red quinonoïd esters

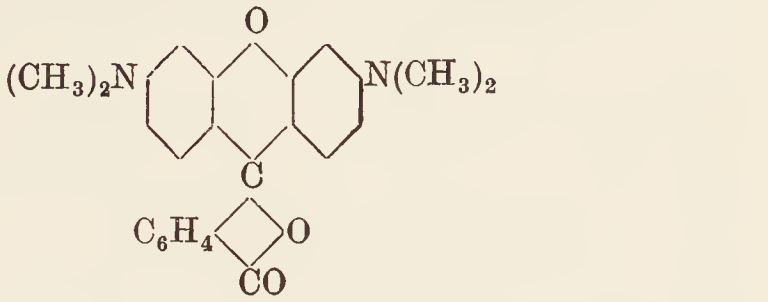
$$C_6H_4(COOCH_3)\cdot C\lessdot{C_6H_4:O \atop C_6H_4\cdot OH}$$

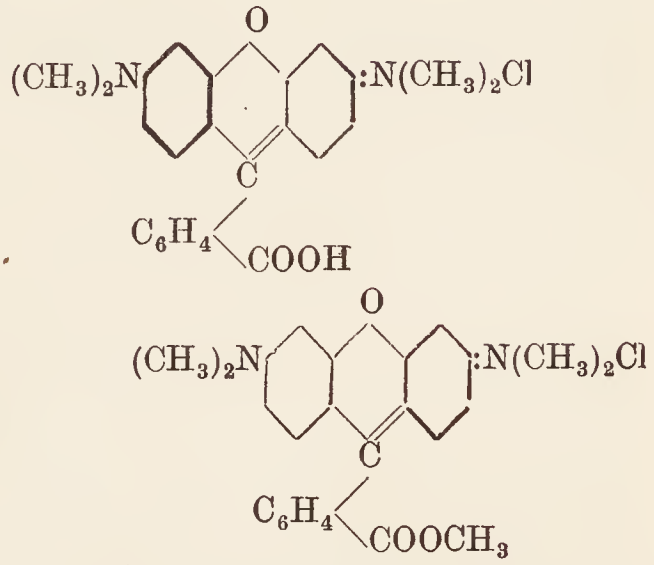
and

$$C_6H_4(COOCH_3)\cdot C\lessdot{C_6H_4:O \atop C_6H_4\cdot OCH_3}$$

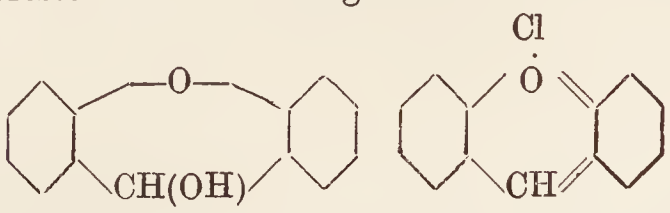
may, however, be obtained (Ber. 1906, 39, 2365; 1907, 40, 3724; Chem. Soc. Proc. 1907, 23, 228; J. Soc. Chem. Ind. 1908, 27, 3; 1909, 28, 63). In these compounds the methyl carboxylate group is very readily hydrolysed. Compare H. Bassett and P. Halton, Trans. Chem. Soc. 1923, 123, 1291.

The rhodamine salts may be esterified and consequently the following formulæ probably represent the relationships existing between rhodamine base, its hydrochloride and the anisoline resulting from its esterification.



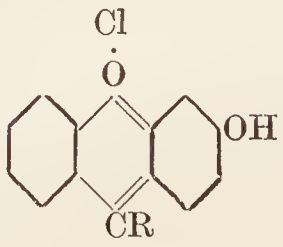


In the case of the salts with mineral acids obtained from fluoresceïn and its parent substance fluorane, an oxonium *o*-quinonoïd structure is probable. The same remark holds in the case of the simpler oxonium salts, and the relationship between xanthydrol and the salt formed from it by hydrochloric acid may be expressed in the following manner:

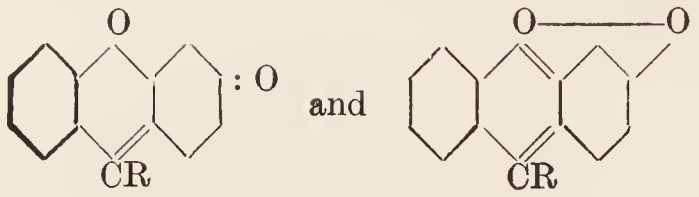


(Hewitt, Zeitsch. physikal. Chem. 1900, 34, 9; Ber. 1901, 34, 3819; Hewitt and Tervet Chem. Soc. Trans. 1902, 81, 663; Werner, Ber. 1901, 34, 3300; Annalen, 1902, 322, 296; Fosse, Compt. rend. 1901, 133, 1218; 1020, 134, 177, and other papers).

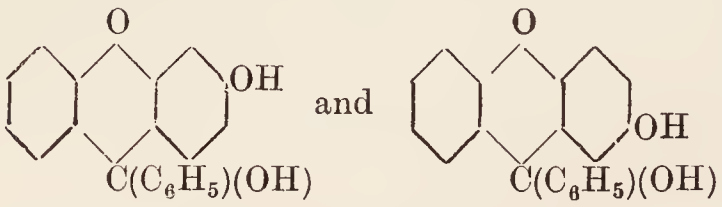
For the salts of the hydroxyanthydrols and fluorones with mineral acids, formulæ such as



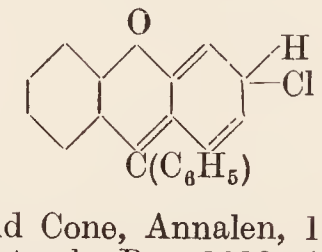
are employed. The free bases lose water, and the formulæ



have been assigned to the anhydrides. Kehrmann favours the second formula (Ber. 1908, 41, 3440). To this Decker raises a grave objection. Of the two compounds represented by



the first is incapable of existence and loses water immediately, whilst the second cannot be dehydrated. If a 'betaine' oxonium phenolate formula is correct, no reason can be assigned for the fact that the second compound retains the elements of water which the first loses spontaneously (Decker, Ber. 1909, 42, 578; compare Pope and Howard, Chem. Soc. Trans. 1901, 97, 1023). Another view as to the constitution of the salts is that they are quinocarbonium compounds, *e.g.*

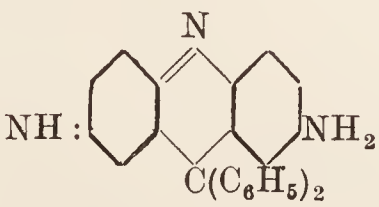


(Gomberg and Cone, Annalen, 1909, 370, 142; compare Hantzsch, Ber. 1910, 43, 339; Kehrmann, Annalen, 1910, 372, 287; Gomberg and Cone, *ibid.* 1910, 376, 183; A. Stepanoff, *ibid.* 1910, 373, 219; Cone and West, J. Amer. Chem. Soc. 1911, 33, 1538).

Acridine and its Derivatives.

Acridine and its derivatives closely resemble the xanthene compounds except that they are more basic, the relationships between bases and salts seem to be similar (Hewitt, A. E. Dunstan and Fox, Zeitsch. physikal. Chem. 1900, 34, 13; Chem. Soc. Trans. 1904, 85, 529; 1905, 87; 1058; 1906, 89, 482, 1472; compare Flürscheim, *ibid.* 1910, 97, 94).

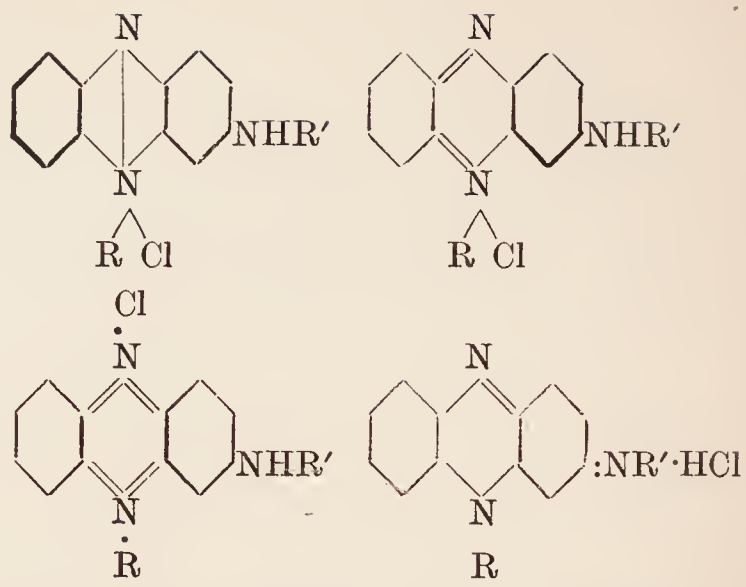
The skeleton of acridine is contained in the carbazine dyes discovered by Kehrmann, Goldstein and Tschudi (Helv. Chim. Acta, 1919, 2, 379). A compound such as



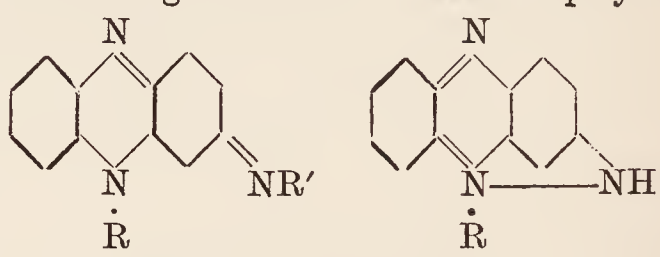
can only be written with a paraquinonoid structure.

Azines.

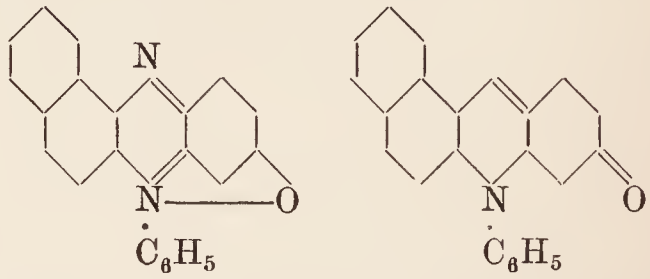
The salts of mono-arylaminoazines will possess one of the following four formulæ



For the corresponding free bases, both of the following formulæ have been employed

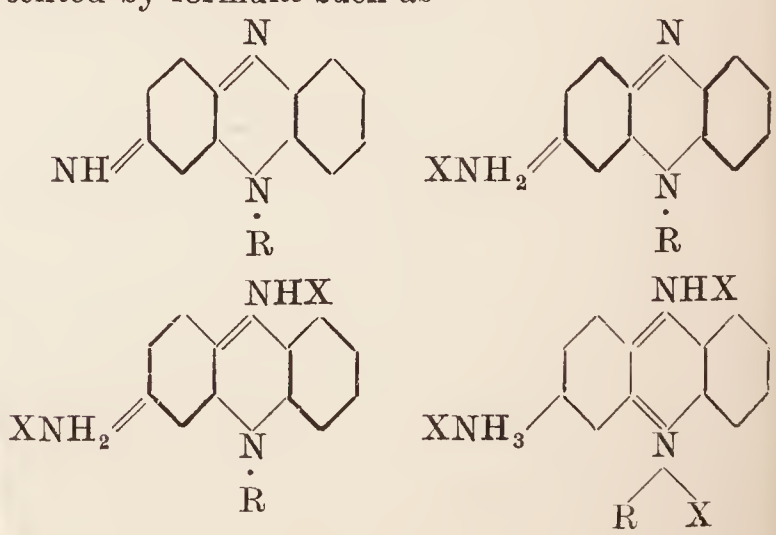


Taking the first formula given for the base and one of the three first formulæ given for the salt, it would appear that there is a rearrangement from para- to ortho- quinonoïd structure on salt formation. With regard to the second formula, Kehrmann has assigned corresponding structures to the safranones, rosindones and *iso*rosindones, thus, for example, in the case of *iso*rosindone he has used a betaïne instead of a *p*-quinonoïd formula



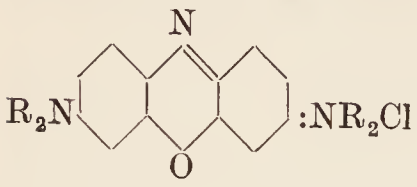
Decker and Würsch (Ber. 1906, 39, 2653) object that *iso*rosindone is not attacked by phenylmagnesium bromide, but Kehrmann (*ibid.* 1908, 41, 12) still held the phenolbetaïne formula to be correct (compare also O. Fischer and Römer, *ibid.* 1907, 40, 3406; Kehrmann, *ibid.* 1908, 41, 472). Many of Kehrmann's views have been considerably modified (Annalen, 1917, 414, 131; Ber. 1920, 53, 63; Helv. Chim. Acta, 1920, 3, 104; 1921, 4, 31, 527; 1922, 5, 69, 895.

Compounds of the type of aposafranine and its moni-, di- and tri-acid salts are to be represented by formulæ such as

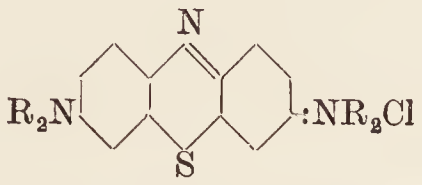


Oxazines and Thiazines.

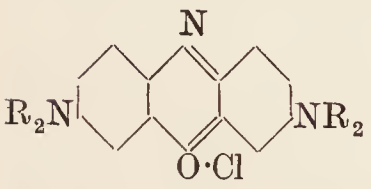
The oxazine and thiazine dyes have been represented by the formulæ

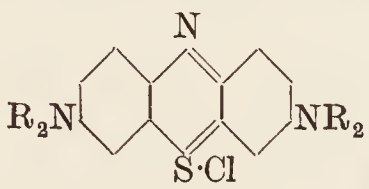


and



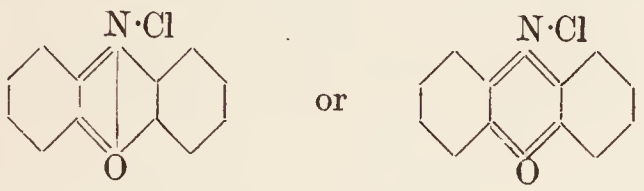
Kehrmann prefers an *o*-quinonoïd structure





representing the compounds as oxonium and sulphonium salts respectively (Ber. 1899, 32, 2601). Considerable discussion has ensued between Hantzsch (*ibid.* 1905, 38, 2146, 2577; 1906, 39, 153, 1365) and Kehrmann (*ibid.* 1905, 38, 2957, 4197; 1906, 39, 914, 1403; 1907, 40, 613, 1234, 1960, 2071).

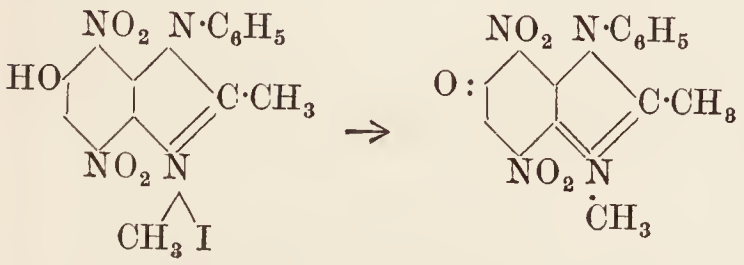
Green suggested *o*-quinonoïd formulæ such as



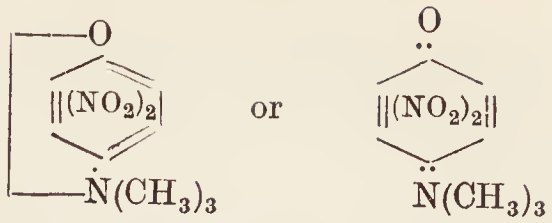
(Ber. 1899, 32, 3155); whilst Hewitt considered it possible that both tautomeric *o*- and *p*-quinonoïd forms exist in solution (Zeitsch. physikal. Chem. 1900, 34, 17). Kehrmann has largely modified his views as to the structure of all 'onium' colour salts as mentioned under the head of azines.

Iminazolium Compounds.

A case of quinonoïd rearrangement of great theoretical interest is afforded by 4 : 7-dinitro-6-hydroxyl-1-phenyl-2 : 3-dimethylbenziminazolium iodide (Meldola and Kuntzen, Chem. Soc. Trans. 1911, 99, 1291). Boiled with water, a substance, $C_{15}H_{16}O_7N_4$ or $C_{15}H_{14}O_6N_4,H_2O$, is obtained; the latter when completely dehydrated loses $2H_2O$. It is difficult to avoid assigning the constitution of a 4 : 7-dinitro-1-phenyl-2 : 3-dimethyl-6-benziminazolone to the dehydrated substance, the initial and final products being represented in the following manner:

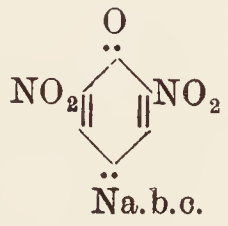


The occurrence of quinquevalent nitrogen in other than ammonium combination is noteworthy and attention should also be paid to the substance



obtained by the extreme methylation of isopicramic acid (Meldola and Kuntzen, *ibid.* 2045), which, together with other alkyl derivatives, has been further examined by Meldola and Hollely (Trans. 1912, 101, 912; 1913, 103, 177; 1914, 105, 410, 977, 1469, 2073; 1915, 107, 610).

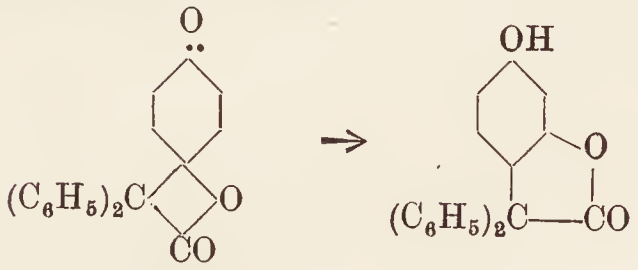
In view of the fact that Meisenheimer has succeeded in resolving oxides of the type O : Na.b.c., it may prove possible to obtain optical isomerides of a substance possessing the structure



Rearrangement from Quinonoid to Aromatic Structure.

Whilst salt formation forces a quinonoïd arrangement, the benzenoïd configuration is the more stable, and many cases have been referred to above in which a substance adds on to a quinone or quinonoïd compound with production of a substituted truly aromatic compound (*e.g.* quinone and hydrogen chloride give chloroquinol).

In addition to such reactions involving addition, a compound of quinonoïd (or more especially semi-quinonoïd) type undergoes intramolecular change with production of a benzenoïd compound. Examples will be found amongst the reactions of the ψ-quinols (production of monoalkyl ethers of 2 : 5-dimethylquinol and dialkyl ether of 4 : 6-dimethylresorcinol from xylo-ψ-quinol), and the production of the ψ-bromides. The transformation of the β-lactones obtained by acting with diphenyl ketone on quinone into a benzenoïd γ-lactone also belongs to this category

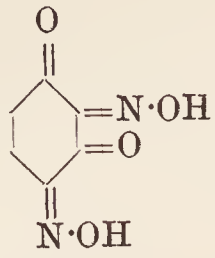


In all these cases we see examples of the tendency of hydroaromatic to pass into aromatic compounds. Reactions of this type are necessarily irreversible. J. T. H.

QUINONEOXIME DYES (*Nitroso colouring matters*). The quinoneoximes can be obtained by two general methods : (1) the condensation of quinones with hydroxylamine; (2) the interaction of nitrous acid and the phenols, the latter process being the one exclusively employed in the commercial preparation of the dyes of this series. These reactions furnish oximes in which the *iso*nitroso group (NOH) is in either the para- or the ortho- position with respect to the remaining quinone oxygen; but only the ortho-compounds are of any value as colour producers. The ortho-quinoneoximes are employed as

adjective dyes in conjunction with iron or chromium mordants on wool, silk, or cotton, the colour being due to the formation of an insoluble lake of the oxime and the metallic base.

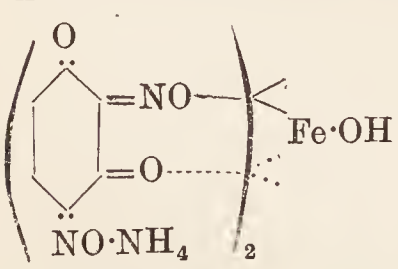
Dinitrosoresorcinol (2 : 4-*dioximinobenzo*-1 : 2 : 3 : 4-*diquinone*), which comes into commerce under the names of **resorcinol green, fast green, Alsace green, dark green in paste, chlorin, fast myrtle green,** is generally represented by the following formula :



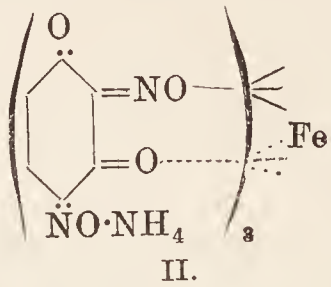
Preparation.—Resorcinol (110 kilos.) dissolved in 4500 litres of ice-cold water containing 120 kilos. of sulphuric acid is slowly treated with 144 kilos. of sodium nitrite (96 p.c.) in 400 litres of water. The product, which separates as a light yellowish-grey precipitate, is washed with water and sold as a 40–50 p.c. paste.

Dinitrosoresorcinol dissolves in hot water or dilute alcohol, crystallises in yellowish leaflets containing $2H_2O$, and decomposes violently at 115° ; it is a moderately strong acid, decomposes carbonates and yields two series of salts ; it loses H_2O on drying *in vacuó* over sulphuric acid. On iron mordanted wool or cotton it yields green shades very fast to soap ; with chrome mordant it gives browns. Dinitrosoresorcinol was formerly used as a basis for resorcinol blue (D. R. P. 14622). When padded on cotton and steamed it furnishes a fast brown dye which serves as a mordant for basic colouring matters (Fitz, Ber. 1875, 8, 631 ; Goldschmidt and Strauss, *ibid.* 1887, 20, 1607 ; v. Kostanecki, *ibid.* 1887, 20, 3137 ; 1888, 21, 1405 ; J. Soc. Chem. Ind. 1890, 1126 ; Rev. gen. mat. col. 1907, 191).

Although green shades are produced with iron mordants, the lakes are in all probability derivatives of ferric iron. With ammoniacal dinitrosoresorcinol ferrous sulphate gives the dark green basic ferric lake I ; ferric alum yields on prolonged treatment the greenish-black normal ferric lake II.

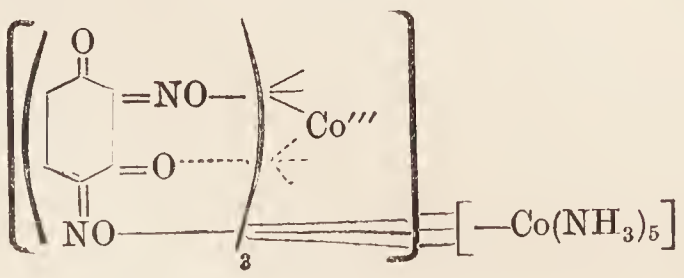


I.



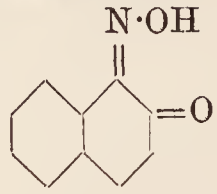
II.

Although containing two *iso*nitroso groups, resorcinol green is a monochelate dye, as is demonstarted by the composition of the cobaltammine lake III, in which only the median *iso*nitroso group is effective in lake formation (Morgan and Moss, Chem. Soc. Trans. 1922, 121).



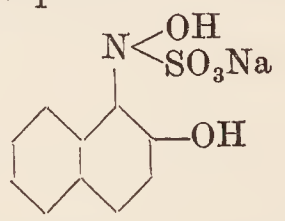
III.

1-Nitroso-β-naphthol (1 : 2-*Naphthaquinone*-1-*oxime*) known as **Gambine Y, Alsace green J, Mulhouse green, Naphthine S.**



Preparation.—β-Naphthol (144 kilos.) is dissolved in 150 litres of hot water containing 48 kilos. of sodium hydroxide, the solution is diluted to 800 litres with ice-water, 72 kilos. of sodium nitrite (96 p.c.) are added and the solution acidified with hydrochloric or sulphuric acid. The yellow precipitate is washed with cold dilute brine solution and made into a 20–30 p.c. paste with water containing a little sodium acetate. The water used in this preparation should be free from iron, otherwise the brown shades produced with chrome mordants are considerably modified. The dilute solution may be acidified before adding the nitrite as the precipitated β-naphthol is so finely divided that it readily reacts with nitrous acid.

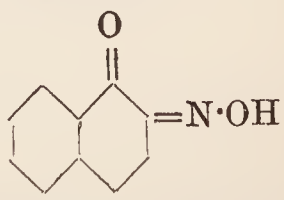
1-Nitroso-β-naphthol crystallises from alcohol or benzene in orange-brown leaflets or prisms, melting at 109°. When quite pure, it can be distilled in steam, but the commercial product generally becomes tarry on boiling with water. Wool and cotton mordanted with iron and chromium give green and brown shades respectively, the former being the faster to light. The bisulphite compound



a grey crystalline paste, produced by mixing 1-nitroso-β-naphthol with aqueous sodium bisulphite, is used for printing a fast green shade on calico mordanted with iron.

The green alkali and ammonium salts of 1-nitroso-β-naphthol have also been employed in dyeing. The insoluble red cobaltic lake is used in the analytical separation of cobalt and nickel. Its constitution as an internally co-ordinated compound has been demonstrated by its quantitative formation on warming to 50°, the hexammino cobaltic salt of 1-nitroso-β-naphthol (Morgan and Main Smith, Chem. Soc. Trans. 1921, 119, 708). The zinc salt is produced by digesting β-naphthol at 60°–70° with an aqueous solution of zinc sulphate and sodium nitrite ; other metallic derivatives may be similarly prepared (D. R. PP. 25469, 78440 ; Fuchs, Ber. 1875, 8, 1026 ; Köhler, *ibid.* 1883, 16, 3080 ; Henriques and Ilinski, *ibid.* 1885, 18, 704 ; v. Kostanecki, *ibid.* 1887, 20, 3147 ; J. Soc. Chem. Ind. 1890, 1126).

2-Nitroso-α-naphthol (1 : 2-*Naphthaquinone*-2-*oxime*) sold as **Gambine R,**



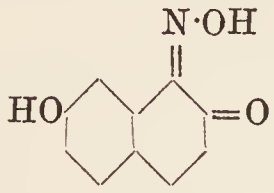
is produced together with its isomeride, 4-*nitroso-α-naphthol* (1 : 4-*naphthaquinone*-4-*oxime*)

by acidifying with hydrochloric acid a cold dilute alkaline solution of α-naphthol and sodium nitrite. The greenish-yellow precipitate is washed and made into a 20–30 p.c. paste.

The isomerides may be separated by taking advantage of their differing solubilities in benzene or by precipitating their alkali salts fractionally from aqueous solution. 4-Nitroso-α-naphthol forms yellowish-white needles, decomposing at 193°–194°; 2-nitroso-α-naphthol, which predominates in the mixture, crystallises from benzene in greenish-yellow needles decomposing at 147°–148° (Ber. 1882, 15, 1816; 1884, 17, 2590; 1885, 18, 706). In practice the crude mixture of the two isomerides is employed in dyeing without removing the inert para- compound.

2-Nitroso-α-naphthol gives green and brown shades on wool mordanted with iron and chromium respectively (references, *v. supra*, 1-nitroso-β-naphthol, and Ber. 1882, 15, 1816; 1884, 17, 2065, 2589).

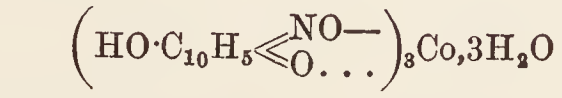
1 - Nitroso - 2 : 7 - dihydroxynaphthalene (7 - *hydroxy*-1 : 2-*naphthaquinone*-1-*oxime*) **Gambine H, Dioxine.**



Preparation.—Naphthalene (500 kilos.) and concentrated sulphuric acid (750 kilos.) are heated at 160°–170° for 6 hours, and the sulphonation carried on for 2 hours longer at 140°–150° with a further addition of 1750 kilos. of acid. The sulphonation product, poured into water, is neutralised with lime and calcium carbonate, the solution of calcium naphthalenedisulphonate is filtered from calcium sulphate, treated with sodium carbonate and crude sodium naphthalenedisulphonate obtained by evaporating the filtered solution to dryness. This sodium salt is added in portions of 150 kilos. to 300 kilos. of fused commercial sodium hydroxide containing about 10 p.c. of added water; the product is acidified with dilute sulphuric acid, the solution boiled to expel sulphur dioxide, then cooled to 4° and treated with aqueous sodium nitrite. The dark reddish-brown precipitate is washed, pressed, and made into 30 p.c. paste with water containing a little sodium acetate.

A purer preparation is obtained by cooling the acidified solution until 2 : 7-dihydroxynaphthalene crystallises out. This compound is then collected and treated in ice-cold water with the calculated amounts of sodium nitrite and dilute acetic acid. Nitroso derivatives have been prepared from the ten isomeric dihydroxynaphthalenes, but only those in which the *iso*-nitroso group is in the ortho- position with respect to the quinone oxygen give coloured lakes on fabrics mordanted with metallic oxides. These nitroso derivatives have the general property of becoming reduced with sodium hydrosulphite to very oxidisable amino-dihydroxynaphthalenes which when absorbed by textile fibres and afterwards exposed to the atmosphere, yield intense shades of brown, grey, and black (Eng. Pats. 1812, 1813, of 1890). The formation of the cobaltic lakes from the ten dihydroxynaphthalenes and sodium cobaltinitrite furnishes a useful qualitative test for these closely related isomeric dihydroxy- compounds, each of which can be identified by the colour reactions of its cobaltic *iso*nitroso derivative (Morgan and Main Smith, *ibid.* 716).

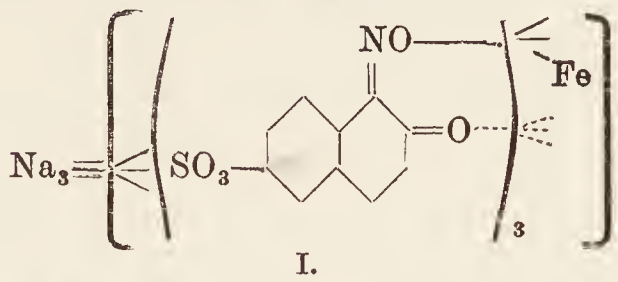
On wool and cotton mordanted with iron salts and dichromate respectively, 1-nitroso-2 : 7-dihydroxynaphthalene gives green and brown shades which are very fast to light. In conjunction with logwood extract and ferrous and copper sulphates it produces a direct black (D. R. PP. 55204, 58611; Eng. Pats. 14230, 17223, 1889; Fr. Pat. 201907; Ber. 1890, 23, 521; 1894, 27, 3050). The purple brown cobaltic lake



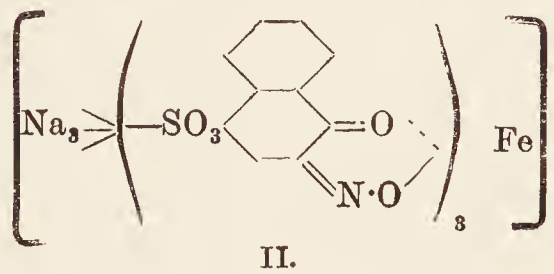
is dehydrated only at 150° *in vacuô*.

The foregoing gambines when condensed with tannic or gallic acid in presence of concentrated sulphuric acid give dyes producing with chrome mordant brown shades which are very fast to light and washing (D. R. P. 75633).

Sodium ferric - 1 - oximino - 1 : 2 - naphthaquinone-6-sulphonate, Naphthol green.



I.



II.

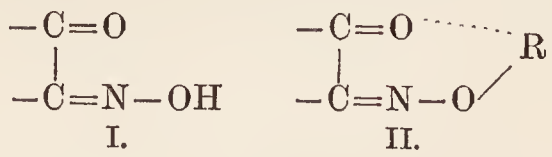
Preparation.—Sodium β-naphthol-6-sulphonate (Schäffer salt) is converted by nitrous acid into sodium 1-oximino-1 : 2-naphthaquinone-6-sulphonate and 27·5 kilos. of this product, dissolved in 100 litres of water, are treated with 20 litres of ferric chloride solution (5 kilos. $FeCl_3$). The excess of iron being precipitated with sodium carbonate, the green filtrate is evaporated to dryness. The double salt (I.) may be purified either by crystallisation from alcohol or through the insoluble lead salt by decomposing the latter with sodium sulphide, carbonate or sulphate.

Wool is dyed green directly in acid baths containing iron salts, and similar shades are produced on silk in the presence of tartaric acid. The colour produced is fast to acids, alkalis, light and milling agents (D. R. PP. 28065, 28901; U.S. Pat. 316036; Eng. Pat. 2296, 1884; Fr Pat. 160032; Ber. 1885, 18, 46; J. Soc. Chem. Ind. 1885, 4, 204; 1890, 9, 1126).

Sodium ferric 2-oximino-1 : 2-naphthaquinone-4-sulphonate, Naphthol Green G (Lev.), which has had considerable vogue as a green mordant dye for wool and silk, is prepared from α-naphthol-4-sulphonic acid in the same manner as its foregoing isomeride. It is more

readily obtained crystalline, and analytical data due to Hoffmann (Ber. 1891, 24, 3741) suggest the formula II. for the green dye. Even ferrous salts lead by aerial oxidation to a ferric lake of basic character (*v. supra*, resorcinol green) and finally to the normal ferric lake II.

The relative stability of the coloured metallic derivatives of the ortho-quinoneoximes containing iron, chromium and cobalt, led Werner to the view that these salts are internally co-ordinated compounds in which the metallic atom is attached to the organic chromophore (I.)

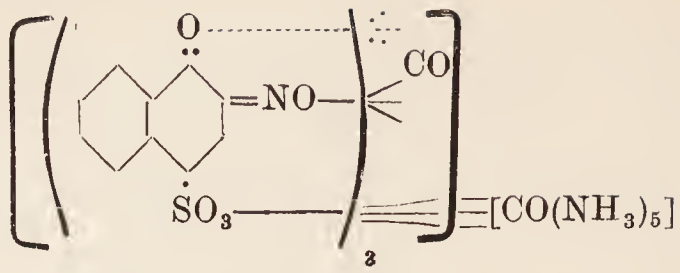


I. II.

by both its principal and secondary valencies so as to produce a stable cyclic complex (II.) in which the metal is not readily detected by the usual qualitative tests. This hypothesis is justified by the fact that the para-quinoneoximes which could not give rise to such six-membered complexes (II.) do not behave as adjective dyes in conjunction with the metallic mordants (Werner, Ber. 1908, 41, 1062, 2383 ; Liebermann, *ibid.* 1436).

Werner's hypothesis that the ortho-quinoneoxime dyes actually contain heterocyclic six-membered rings (II.) involving the mordanting metal has been established experimentally by a study of the cobaltammine lakes of these colouring matters.

When reacting with cobaltammine reagent $[CO{\cdot}OH,5NH_3]Cl_2$ in aqueous ammonia the chromophoric radicle or chelate group I. gives rise to a cobaltic lake in which the metallic atom is incapable of further co-ordination. Any other salt-forming group present in the dye, such as OH,CO_2H or SO_3H, furnishes a cobaltammine lake containing $5NH_3$. Thus the complex cobaltammine lake from naphthol green G has the constitution III. where



III.

of two cobalt atoms only one is capable of co-ordinating externally with ammonia. In a complex lake from nitroso chromotrope acid there are four cobalt atoms but only three give pentammine co-ordination. This difference between the cobalt atom of the chromophoric (chelate) group and the cobalt atoms of the ordinary salt-forming groups is generalised in the simple equation

$$m=5(n-1)$$

where m and n represent ammonia molecules and cobalt atoms respectively (Morgan and Main Smith, Chem. Soc. Trans. 1921, 119, 707).

G. T. M.

QUINOPYRIN. Trade name for a mixture of antipyrine and quinine hydrochloride.

QUINOSOL *v.* Chinosol.

QUINOTANNIC ACID *v.* Tannins.

QUINOTROPIN. A compound of quinic acid and hexamethylene tetramine. Used as a uric acid solvent.

QUINOVIN *v.* Glucosides.

QUINOXALINES *v.* Azines.

QUINOXIMES *v.* Azines.

QUISQUEITE. A lustrous, black, brittle substance, very like asphaltum in appearance, but containing much sulphur (S 46½ p.c. with C 43 p.c.) and only little hydrogen. Sp.gr. 1·75. It occurs in considerable quantity, together with patronite (*q.v.*), in a deposit of vanadium ore in the Quisque (or Minasragra) district, near Cerro de Pasco in Peru. (*See* W. F. Hillebrand, Amer. J. Sci. 1907, 24, 141 ; D. F. Hewett, Trans. Amer. Inst. Mining Engin. 1910, 40 (for 1909), 274.) L. J. S.

R

R ACID. 2-Naphthol-3 : 6-disulphonic acid *v.* Naphthalene.

2 R ACID. 2-Amino-8-naphthol-3 : 6-disulphonic acid *v.* Naphthalene.

RACEMIC ACID *v.* Tartaric acid.

RACEMISM. The phenomenon of racemism has reference to the existence of inactive compounds or double salts of two optical enantiomorphs, which differ in certain physical and chemical properties from either active component singly or mixed in equal quantities.

Historical.—Racemism was first observed by Pasteur (Leçons sur la Dissymmétrie Moléculaire, 1861 ; Researches on Molecular Asymmetry, Alembic Club Reprints, No. 14) in studying the crystalline forms of tartaric and racemic acids and their salts. He discovered hemihedral facets on the sodium ammonium salt of tartaric acid, and concluded that this property might be related to its rotatory power, the acid being dextrogyrate. If this were the case, then racemic acid and its salts, being optically inactive, should exhibit no such facets. To test this conclusion, he performed his well-known experiment, which consisted in crystallising sodium ammonium racemate. The result was that instead of an inactive salt without hemihedral facets, he succeeded in resolving the substance into two forms having hemihedral facets on obverse sides of the crystal, and each kind when separately dissolved and examined showed rotatory polarisation in the reverse direction.

W. Staedel (Ber. 1878, 11, 1752) who afterwards repeated the experiment only obtained the original racemate. It therefore appears that the same substance may under certain conditions crystallise as a double salt, and under others may break up into two active components.

Scacchi (Rend. Accad. Sci. Fis. Mat. Napoli, 1865, 250) had already explained the cause of Staedel's failure by showing that the racemate separates from solution at a higher temperature than the active tartrates. Wyrouboff (Compt. rend. 1886, 102, 627) found this temperature to lie above or below 28°, and later van 't Hoff and van Deventer (Zeitsch. physikal. Chem. 1887, 1,

173) were able to show that it coincided with the transition temperature at which the tartrates lose water of crystallisation and pass into the racemate.

$2C_4H_4O_6NaNH_4,4Aq = (C_4H_4O_6NaNH_4,2Aq)_2 + 6H_2O$
Sodium amm. tartrate. Sodium amm. racemate.

As the change is accompanied by change in vapour pressure of the saturated solutions and in the volume of the crystals, these observers were able to fix very accurately by tensimeter and dilatometer measurements the transition temperature, which they found to be 26·7°–27·7°.

Examples of the same phenomenon have been observed in the case of other salts of tartaric acid, also of malic acid and other substances.

	Transition temp.
Sodium potassium tartrate	—6°
Potassium tartrate	37·2°
Rubidium ,,	40·4°
Ammonium bimalate	74°
Methyl mannoside.	8°
Camphoroxime	103°

Properties of racemic compounds.—Racemic compounds differ in the following physical and chemical properties from their active components:—

1. *Crystalline form.*—Many active substances crystallise in a different system from the racemic form: the former often exhibiting hemihedral facets, whereas the latter is usually holohedral.

2. *Specific gravity* of the two crystalline substances is different.

Substance	Specific gravity Active	Racemic
Limonene tetrabromide	2·134	2·225
Carvoxime	1·108	1·126
Fenchoneoxime	1·117	1·142
*iso*Fenchoneoxime	1·134	1·180
Carvonetetrabromide	2·242	2·249
Carvonetribromide	1·958	1·958
Sobrerol	1·128	1·131

From the above table it appears that the racemic compounds have, as a rule, the greater specific gravity (Liebisch, Annalen, 1895, 286, 140; Walden, Ber. 1896, 29, 1699).

3. *Solubility and melting-point.* — There appears to be a certain relation between the solubility and melting-point on the one hand, and the specific gravities on the other, of the racemic and active forms. If the specific gravity of the racemic compound is greater, the melting-point is higher and it is also less soluble. If the specific gravity is less, the melting-point and solubility are reversed. The following examples exhibit these relationships.

	Sp.gr.		M.p.		Solubility	
Substance	*a.*	*r.*	*a.*	*r.*	*a.*	*r.*
Malic acid	1·595	1·601	100°	130°–131°	greater	less
Camphoric acid	1·186	1·228	187°	202°–203°	greater	less
Tartaric acid	1·754	1·697	170°	204°	greater	less
Mandelic acid	1·341	1·300	130°	118°–119°	less	greater

4. *Absorption spectra.*—These have been shown by Stewart to be different in the active and racemic forms.

5. *Water of crystallisation.*—It is a common observation that the active and racemic forms usually contain different amounts of water of crystallisation.

Substance	*a.*	*r.*
Tartaric acid	—	H_2O
Ammonium tartrate	—	$2H_2O$
Potassium ,,	$\frac{1}{2}H_2O$	$2H_2O$
Thallium ,,	$\frac{1}{2}H_2O$	—
Sodium ,,	$2H_2O$	$2H_2O$
Potassium lithium tartrate	H_2O	H_2O
Potassium antimonyl ,,	$\frac{1}{2}H_2O$	$\frac{1}{2}H_2O$
Strontium glycerate	$3H_2O$	$\frac{1}{2}H_2O$
Barium ,,	$2H_2O$	$\frac{1}{2}H_2O$
Calcium galactonate	$5H_2O$	$2\frac{1}{2}H_2O$
Barium ,,	$5H_2O$(?)	$2\frac{1}{2}H_2O$

6. *Physiological properties.* — Chabrié has shown that racemic acid is less poisonous than the active tartaric acids, and Tiemann and Schmidt noticed that inactive terpenes often have a fainter odour than the active forms.

In dilute solution the racemic compound dissociates into its two active components and consequently the solution behaves like a mixture of the two enantiomorphs. It has no action on polarised light, and such properties as vapour pressure, specific gravity, magnetic rotation and electrical conductivity (in the case of an acid) are identical with those of a mixture of the active components. The vapour density is also the same. Thus, Anschütz (Ber. 1885, 18, 1397) has shown that ethyl racemate is monomolecular when vaporised.

Methods of distinguishing racemic compounds from mixtures.—The criteria for determining whether an inactive, crystalline substance is (1) a mixture or *conglomerate* of equal quantities of the two kinds of crystals not forming a compound; (2) a true *racemic compound*, that is, a compound consisting of equal molecules of the two enantiomorphs; or (3) an isomorphous mixture or mixed crystal (called also a *pseudo-racemic compound*), have been examined by Bakhuis Roozeboom (Zeitsch. physikal. Chem. 1899, 28, 494) from the standpoint of the phase rule, and he has shown that the melting-point and solubility afford the most trustworthy evidence of racemism.

Melting-point of conglomerates.—In this case each enantiomorph must be regarded as a separate individual and the melting-point of each (when present in excess, it may be regarded as the solvent) will be lowered by the addition of the second enantiomorph, the eutectic or mixture of minimum melting-point being reached when both are present in equal quantity. The melting-point curves of the two enantiomorphs will have the following form:—

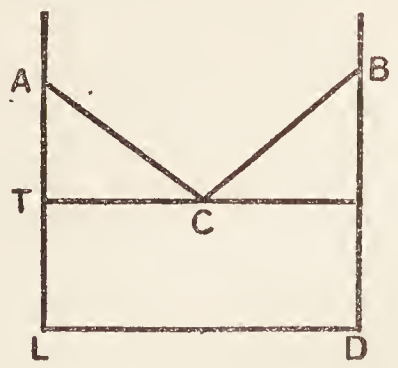


Fig. 1.

If A and B represent the melting-point of the pure lævo- and dextro- enantiomorphs (L and D),

AC and CB will represent the melting-point curves of each of the enantiomorphs when mixed with increasing proportions of the other, and C the melting-point of the inactive mixture when equal quantities of the two are present. Consequently when either enantiomorph is added to the conglomerate the melting-point will be *raised*.

Melting-point of racemic compounds.—The melting-point curve of a racemic compound and its two enantiomorphs will form three curves, for there are three individuals, and according to whether the racemic compound has a higher or lower melting-point than the enantiomorphs the curves will take the following forms :—

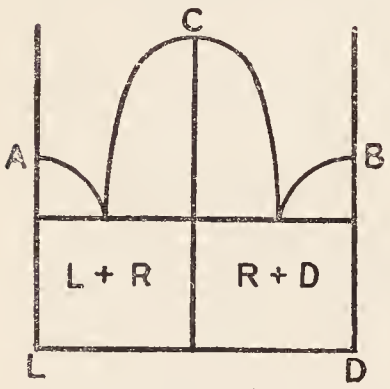


Fig. 2.

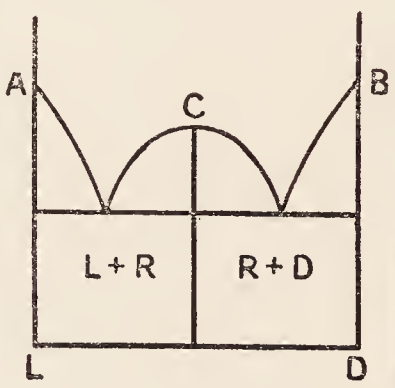


Fig. 3.

Thus active dimethyl tartrate melts at 43·3° ; racemic dimethyl tartrate at 89·4°, and the curve would take form represented in Fig. 2, whilst active mandelic acid melts at 132·8° and the racemic acid at 118° and would have the form shown in Fig. 3. Here the addition of a small amount of either enantiomorph to the racemic compound will *lower* the melting-point.

Melting-point of pseudoracemic mixed crystals.—If the two enantiomorphs are isomorphous and form mixed crystals they form only a single phase and the fusion-point will depend upon the composition of the solid which separates from the fused mass. If it is identical with that of the fused mass, a constant melting-point for any mixture is obtained. This has been observed in the case of the two active camphoroximes. The curve is then a horizontal line joining the melting-points of the enantiomorphs, Fig. 4.

This property is exhibited by 1-amyl-3-nitrophthalates ; the compounds themselves and mixtures melt at 116°, also by 2-amyl-3-nitro-

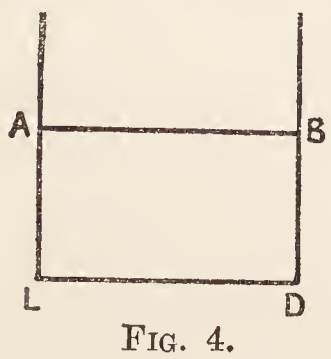


Fig. 4.

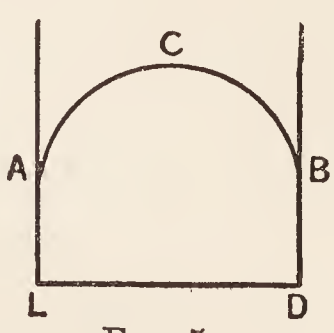


Fig. 5.

phthalates which melt at 155°, and amyl phenylcarbamates which melt at 31° (W. Marckwald and Nolda, Ber. 1909, 42, 1583).

If, on the other hand, the solid which separates differs in composition from the fused mass, the melting-point curve will be either convex or concave. The former, Fig. 5, will occur when the concentration of the second enantiomorph in the separated solid is less, the latter, Fig. 6, when it is greater than in the fused mass. The curve in both cases will be a continuous one and reach its maximum or minimum at C when equal quantities of both enantiomorphs are present. A maximum, 91·4°, has been observed in the case of the carvoximes, the enantiomorphs melting at 72° ;

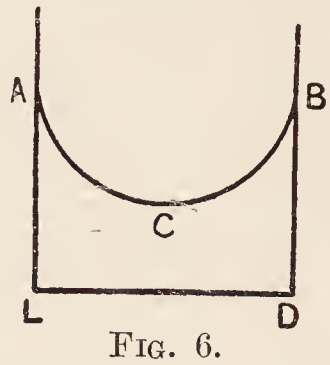


Fig. 6.

and a minimum in that of *d*- and *dl*-amyl carbamates (W. Marckwald and Nolda, Ber. 1909, 42, 1583).

The above criteria in regard to the nature of an inactive substance only hold in the neighbourhood of the melting-points. At other temperatures, transformations may occur of a racemic compound to a pseudoracemic compound or a conglomerate or *vice versa*.

Solubilities of racemic compounds and mixtures.—The phase rule may also be applied to the equilibrium between a racemic compound or mixture and its saturated solution in precisely the same way as to a mixed and double salt (Bakhuis Roozeboom, Zeitsch. physikal. Chem. 1899, 28, 494). A system consisting of a mixture of the dextro- and lævo- enantiomorphs in equilibrium with a saturated solution is a 3-component system and is invariant for a given temperature. The isothermal solubility curve of each will vary (increase or decrease) with each addition of the other enantiomorph until a maximum or minimum solubility point is reached when both are present in equal quantity, that is, when an inactive mixture is formed. If either enantiomorph is now added no change will result, for the solution is saturated in regard to each enantiomorph and neither will be dissolved. In Fig. 7, if the vertical represents the concentration of

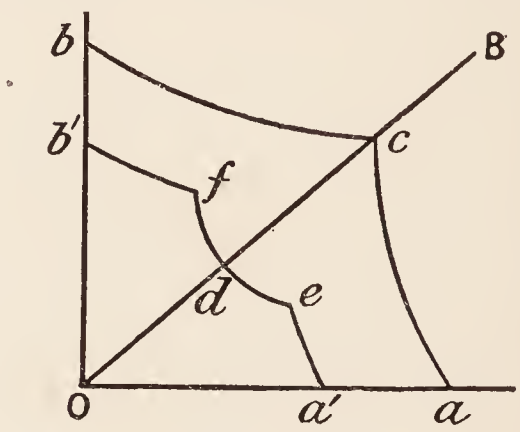


Fig. 7.

the lævo- and the horizontal that of the dextro-enantiomorph, the upper solubility curve *acb* represents that of a mixture (above or below the transition point of the racemic compound). The point *c* will lie on the line OB equidistant between the horizontal and vertical, since the two enantiomorphs possess identical solubilities. The solubility curve for the pure racemic compound will also cut

the line OB either above or below *c*, depending on the transition temperature and, as in the former case, the point will be a maximum or minimum according to whether the solubility of the racemic compound increases or decreases in presence of excess of either enantiomorph. The curve *a′efb′*, in Fig. 7, represents the solubility curve for rubidium racemate, the transition point of which lies below that of the conglomerate. The addition of an excess of either enantiomorph will introduce a new phase and a new equilibrium will be established which will lie on *df* or *de* according to the enantiomorph added; in other words, the solubility will be different from that of the pure racemic compound, and moreover some of the active component will pass into solution. Thus, by comparing the concentrations of the saturated solutions before and after addition of the enantiomorph, it would be possible to ascertain whether the original substance were a racemic compound or a conglomerate. Moreover, the addition of either enantiomorph to the solution of the racemic compound would produce an optically active solution which could be readily observed in the polarimeter. These facts have been demonstrated experimentally by Kendrick (Ber. 1897, 30, 1749) in the case of *r*-ammonium bimalate.

Partial racemism.—The term is applied to those cases in which a double salt is formed, consisting of equal molecules of two active components which are not enantiomorphs. The phenomenon was first observed by Pasteur, who obtained crystals of a double salt of ammonium *d*-tartrate and ammonium *l*-malate. Another form of combination to which Ladenburg first applied the term *partially racemic* compound was observed by him in the case of quinine pyrotartrate, which forms three series of salts, from one of which the *d*-acid, from a second the *l*-acid, and from a third the inactive acid was separated. The quinine in the third case must therefore have united with the unresolved racemic acid or, what amounts to the same thing, a double salt of quinine *d*- and *l*-tartrate must have been formed.

An example of a similar kind was observed by Pope (Chem. Soc. Trans. 1898, 73, 902) in which the inactive base, *r*-tetrahydropapaverine, was found to form a double salt with *d*-tartaric acid. In the above cases, the solutions will be active and the two components will have different melting-points and solubilities. Consequently, neither melting-point nor solubility curves will be symmetrical. In the latter case the curve will resemble that of an ordinary double salt. If it lies beyond the transition point, the point of maximum or minimum solubility will not lie on OB and the addition of either enantiomorph to the solution of the original material would effect no change. Similarly if the solubility curve were drawn below the transition point it would have the form *a′efb′* shown in Fig. 8, and three different solutions could be obtained corresponding to *e*, *d* and *f*, that is, the addition of either enantiomorph to the partially racemic compound would alter the concentration as in the case of the racemic compound.

Racemic liquids.—The question of the existence of racemic liquids has frequently been discussed. Ladenburg found that by mixing *d*- and *l*-conine a decrease of temperature of 1·4° was observed and concluded that the product

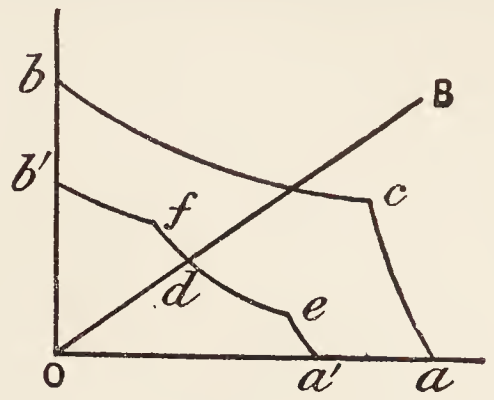


FIG. 8.

was a racemic liquid. As the mixing of two enantiomorphs would produce no change of temperature, unless change of internal energy followed by combination of some kind had occurred, Ladenburg was probably correct in supposing that a racemic compound was formed; but the experiment does not prove that the whole product is racemic (A. Meyerhoffer, Gleichgewichte der Stereomeren, Leipzig, 1906). That such an equilibrium mixture of conglomerate and racemic compound can exist in a fused state follows from a study of the temperature-pressure curves of racemic and tartaric acid, the fusion curves of which must be continuous. There is nothing surprising in the fact that the magnetic rotations of ethyl tartrate and racemate are identical (Perkin, Chem. Soc. Trans. 1887, 51, 368) as this property is determined only by the number and kind of atoms. The same applies to specific rotation (Pope and Peachey, Chem. Soc. Trans. 1899, 75, 1117). The density of ethyl tartrate and racemate and other active and racemic liquids (such as conine and tetrahydroquinoline) are also identical. The same appears to be true of the boiling-point. Limonene and dipentene and active and racemic malic ester, however, show small differences of 1° or 2°. The solubilities of active and inactive liquid carvoxime in alcohol are the same (van der Linden, Ber. 1911, 44, 963; Kruyt, *ibid.* 1911, 44, 995; Ladenburg, *ibid.* 1911, 44, 1677).

The observation that the rate of decomposition of camphor carboxylic acid in acetophenone solution is 3 p.c. less when a mixture of *d*- and *l*-acids is used than when either is present alone seems to offer evidence of the existence of racemic compounds in the liquid state or in solution (Fajans, Zeitsch. physikal. Chem. 1910, 73, 25). J. B. C.

RACHITOL *v.* SYNTHETIC DRUGS.

RACK-A-ROCK *v.* EXPLOSIVES.

RADDLE. A kind of red ochre *v.* REDDLE.

RADIOLOGY.

I.—RADIOACTIVITY.

(A) *Radioactive Substances.*

§ (1) **Discovery.** The science of radioactivity dates from the year 1896, when H. Becquerel made the important discovery that uranium salts *spontaneously* emit radiations capable of affecting photographic plates and of penetrating considerable thickness of matter (Compt. rend. 1896). The radiation did not decrease with time, and its intensity was independent of the physical conditions to which

the uranium was subjected. The radiations also produced phosphorescence in certain materials, such as zinc sulphide and ionised gases through which they passed. By an examination of various compounds containing uranium Mme. Curie was able to show that the intensity of the radiation depended only on the amount of uranium in the specimen examined, and not on its composition. The name *radioactivity* was given to the newly-discovered property of uranium. In 1898 it was shown independently by G. C. Schmidt (Wied. Ann. 1898, 65) and by Mme. Curie (Compt. rend. 1898) that the property of radioactivity was shared by thorium compounds and minerals containing that element. A little later Mme. Curie showed that the content of different minerals in radioactive material varied greatly, and that some minerals were even more active than metallic uranium. Such was the case with pitchblende from Joachimstal, and it therefore seemed that the radioactivity of this mineral could not be entirely ascribed to uranium.

§ (2) **Radium, Polonium, and Actinium.** Further investigations by M. and Mme. Curie led to the chemical separation of highly radioactive substances from pitchblende, with the result that two new radioactive elements, *polonium* and *radium*, were discovered (Recherches sur les Substances Radioactives, 2nd ed., Paris, 1904). A third radioactive element, *actinium*, was subsequently isolated from pitchblende by Debierne (Compt. rend. 1899 and 1900). The method of separating these elements from pitchblende consisted in subjecting the mineral to certain chemical reactions and examining with an electroscope the radioactivity of the products obtained. The method, in fact, was one of ordinary fractionation in which chemical tests were replaced by electroscope measurements. The three new radioactive elements polonium, radium, and actinium, are precipitated, respectively from uranium ores with bismuth, barium, and certain rare earths, notably thorium. Such precipitations formed the starting-point for the separation of these bodies, but as the new elements closely resemble the elements with which they are precipitated, their further purification was a matter of considerable difficulty. Ultimately, however, very active preparations of salts of all three elements have been prepared, and in the case of radium, in sufficient quantity and in a state of sufficient purity for atomic weight determinations to be made. In some early experiments Mme. Curie found the value 225 for the atomic weight of radium, and in later experiments 226·2 (Compt. rend. 1907, 145). Thorpe has also made a determination, and gives the value 227 (Proc. Roy. Soc. 80, 1908). O. Hönigschmid (Wien. Akad. Anzeiger, 1911, 19, 1), from a series of concordant determinations in which from 0·6 grm. to upwards of 1 grm. of $RaCl_2$ were employed, found that Ra=225·95 (Ag=107·88 and Cl 35·457). The spark spectrum of radium has also been examined by Demarcay (Compt. rend. 1898, 127; 1899, 129; and 1900, 131) and others, and the flame spectrum by Giesel (Phys. Zeitsch. 1902, 3). Both spectra have been carefully studied by Runge and Precht (Annalen Phys. 1903, 10; 1904, 14). The spectrum of radium shows certain important similarities to those of magnesium, calcium, strontium, and barium, to which group of elements radium belongs. Pure metallic radium has been isolated by Curie and Debierne (Compt. rend. 1910, 151), and an amalgam of the metal is known (Coehn, Ber. 1904, 37).

§ (3) **Radioactive Emanations.** It was found that when measuring the ionisation produced by thorium, the results were greatly disturbed when air currents were set up in the vessel containing the thorium. These disturbances were traced by Rutherford to the fact that thorium salts continuously emit a temporarily radioactive gas, which he named an *emanation* (Phil. Mag. Jan. 1900). Similar radioactive gases have since been shown by Dorn to be given off by radium (Abhandlungen der Naturforscher-versammlung zu Halle, 1900), and a similar emanation has been found by Debierne from actinium (Compt. rend. 1903, 136). The activity of all these gases is not permanent, but falls off in geometrical progression with time, indicating that some change is proceeding which follows the same law as a monoatomic chemical reaction. The activity of the actinium emanation decays so quickly that after 3·9 seconds it has fallen to half its original value. The thorium emanation takes 54 seconds to lose half its activity, and the activity of radium emanation is much more permanent, falling to half value in 3·85 days. The properties of the emanations are in many ways analogous, but on account of the slow decay of its activity more is known about radium emanation than about those from thorium or actinium. The rate of evolution of the emanation from radium depends largely on the physical state of the radium salt. Thus, if very carefully dried, less emanation is evolved than when the salt is moist. A solution of a radium salt evolves emanation still more freely and by boiling can be completely deprived of the emanation contained in it. When the emanation has been expelled, the salt is said to be *de-emanated*. De-emanation can also be effected by heating a radium salt to about 800°. It thus appears that only a definite quantity of emanation can be extracted at any time from a given quantity of radium; but it is found that the radium gradually regains its power of emanating. After 3·85 days half the original amount of emanation can again be drawn off, and after the lapse of some weeks as much emanation can be collected as was originally extracted. While the radium is regaining its emanating power, the emanation gradually loses its activity, and it is found that at any time the sum of the activities of the emanation which has been separated from the radium and that which is unseparated is constant. The explanation of this fact will be given later. Radium emanation can be collected in comparatively large quantity, so that its chemical and physical properties can be studied. It is a matter of great difficulty to purify the emanation from other gases, but by special methods this can be done. By a somewhat indirect method it has been shown by Rutherford and Geiger that it should be possible to extract from one gram of pure radium 0·585 cubic mm. of pure emanation (Proc. Roy. Soc. 1908, 81). This value has been found by direct

experiment to be correct by Ramsay and Soddy (*ibid.* 1903, 72) and Rutherford (Phil. Mag. 1908).

§ (4) **Nature of Emanation.** The nature of the emanation has been carefully studied, and it has been shown to behave in every way exactly as an ordinary gas. It can be condensed to a liquid by cooling, and its boiling-point is given by Rutherford and Soddy as −150°C. under ordinary conditions when mixed with air (*ibid.* 1903). When purified its condensation point rises with increase of pressure, and becomes −65° at atmospheric pressure (Rutherford, *ibid.* 1909). The emanation also diffuses as other gases, and dissolves in liquids, and Boyle has shown that it obeys Henry's law of solution (*ibid.* 1911). The spectrum of the emanation has been mapped by Rutherford and Royds (*ibid.* 1908). The value of the atomic weight of radium emanation can be predicted from theoretical considerations as 222. A direct determination by Gray and Ramsay gives 220 (Proc. Roy. Soc. 1911, 84). Chemically the emanation behaves as an inert gas, and seems to be monatomic and to belong to the argon family. The properties of thorium and actinium emanations have not been so fully studied, on account of the difficulty of obtaining sufficient quantities of these gases, but there is every reason to believe that they have similar properties.

§ (5) **The Active Deposits.** In an important investigation Curie has shown that bodies brought into the neighbourhood of radium themselves become temporarily radioactive, having acquired the property of emitting radiations even when removed from the presence of the radium (Compt. rend. 1899, 129). The bodies were said to have had radioactivity *induced* or *excited* in them. Analogous phenomena were discovered by Rutherford for thorium (Phil. Mag. 1900) and by Debierne for actinium. The activity so induced was soon shown to be transferred to the bodies made active by the emanations escaping from the radioactive sources. The activity produced was only temporary as with the emanations, but the rates of decay were different from those of the emnanations and characteristic of the element inducing the activity. Subsequent experiments have shown that bodies made active in this way could be deprived of their activity by mechanical means such as rubbing on a rough surfacc, or, chemically, by immersion in hydrochloric or nitric acid. Also by strongly heating the surface, the activity was removed. It therefore appeared that induced activity is due to the deposition of radioactive matter; the name 'induced activity' has therefore been abandoned and replaced by the name *active deposit.* When produced from the emanation in an electric field, the active deposit is in most circumstances concentrated on the cathode; a small amount is, however, usually also found on the anode. Recent experiments by Ratner show that the ratio of the amounts of active deposit carried to cathode and anode respectively is largely influenced by the 'electric wind' produced by the field (*ibid.* 1917). The decay of activity of the active deposits is complicated, and depends on the conditions of deposition, but after the lapse of some hours the activity decays in a geometrical progression with time, falling to half value in 27 minutes for radium, 36 minutes for actinium, and 10·5 hours for thorium.

§ (6) **Disintegration Theory.** (i) *General outline.*—The phenomena described show that the elements radium, thorium, and actinium spontaneously give rise to a number of different forms of radioactive matter with definite chemical and physical properties, and the processes involved seem to take place independently of external conditions. To explain these facts the theory has been put forward by Rutherford and Soddy, that radioactivity is due to the disintegration of the radioactive elements, and that the radiations emitted are the manifestation of this process (*ibid.* 1902). Thus, in the case of radium, the atoms are slowly but continuously breaking up, and at each disintegration of an atom an α particle is evolved, so that there is formed a new atom, the emanation, with a lower atomic weight possessing chemical and physical properties different from those of radium. The atoms of emanation in turn break up, giving rise to the active deposit. The latter has been shown to consist of a complicated mixture of products formed consecutively as the result of a series of atomic disintegrations. These are known respectively as radium A, B, C, D, E, and F.

(ii) *Radioactive constant and half-value period.*—A mathematical theory, based on the above assumptions, has been worked out, and has been of the greatest service in analysing the complicated phenomena involved in radioactive transformations. In a simple transformation the activity falls off as a geometrical progression with time, and we have the relation $N=N_0e^{-\lambda t}$, where N_0 is the number of atoms of active matter present at the beginning, N the number present at any subsequent time t and λ is a constant characteristic of the particular atom considered. Differentiating the above equation, it is seen that p, the rate of disintegration of the matter, is given by $p=\frac{dN}{dt}=\lambda N$ so that λ which is known as the *radioactive constant*, represents the fraction of the total number of atoms disintegrating per second. The quantity $\frac{1}{\lambda}$ is sometimes taken as defining the rate of decay of a radioactive element, and is called its *mean life.* It is more usual to define the rate of decay by the time taken for the number of atoms present to decrease to half their original number. This time τ is connected with λ by the relation $\tau=\frac{1}{\lambda}\log_e 2=0{\cdot}693\frac{1}{\lambda}$. This quantity is called the *half-value period* of the product. It must be understood that the above equations give a statistical representation of the phenomena, and are only true when the number of atoms involved is large compared with the number breaking up per second. In this case the laws of probability apply, but if the number of atoms is small, this is no longer the case.

(iii) *Radioactive equilibrium.*—From a knowledge of the way in which a radioactive product decays, its rate of growth from a constant source of supply can be calculated. As an example may be taken the case of radium which disintcgrates so slowly that the number of atoms present does not vary sensibly over

a short time. Suppose that the radium has been de-emanated, it is required to find the quantity of emanation present in the radium at any subsequent time. Let q be the number of atoms of emanation produced from the radium per second, and let N be the number of atoms present after a time t. Then $\frac{dN}{dt}=q-\lambda N$, where λ is the radioactive constant of the emanation; for the number of atoms of emanation disintegrating per second is given by λN. After a long time when the number of atoms of emanation formed equals the number breaking up, the emanation will have come into equilibrium with the radium; there will then be some definite number N_0 of atoms of emanation present. By integrating the above equation we get $N=N_0(1-e^{-\lambda t})$, since when $t=0$, $N=0$, and when $t=\infty$, $q=\lambda N_0$; for ultimately the number of atoms of emanation disintegrating becomes equal to the number formed from the radium. When this stage is reached a state of *radioactive equilibrium* is said to have been set up between the two products. It will be seen that the equation giving the rise of the number of atoms of emanation from de-emanated radium is complementary to that for the decay of the emanation, showing that the total number of atoms of emanation equivalent to a definite quantity of radium is constant, whether it is associated with the radium or has been separated from it. The processes which have been exemplified by the case of radium hold generally for all radioactive bodies, but the decay constants are different in every case. A general expression has been given by Bateman for the number of atoms of any product present at any time in a series of successive products if the number of atoms of each product present at some fixed time is known (Proc. Camb. Phil. Soc. 1910, 15).

§ (7) **Separation of Radioactive Products.** The disintegration theory frequently gives a means of detecting new products and of estimating their radioactive constants; but it is often necessary to separate products from each other to examine them alone under simple experimental conditions. There are three ways of doing this. Firstly, by chemical means which can be exemplified by the first separation made by Crookes (Proc. Roy. Soc. 1900, 66). Uranium can be precipitated from its salts by addition of ammonium carbonate; the precipitate is, however, dissolved by excess of the reagent, but a strongly radioactive light brown residue containing iron and other impurities is left in suspension. The activity decays to half value in 22 days, showing that the residue contains a product which has been called uranium X (*q.v.*). There are many other cases of such chemical separations which might be cited. A second method of separating products is by fractional distillation. Most of the radioactive products boil at high temperatures, though there is evidence in many cases of volatilisation even at ordinary temperatures. By heating to a suitable temperature a separation of two or more products can therefore be effected. A third way of separating successive radioactive products is by the method of *recoil*. When an atom emits an α particle, the residual atom constitutes the product next in the radioactive series. Now, since the α particle possesses considerable momentum, the residual atom receives a shock sufficient to carry it some distance in a direction opposite to that in which the α particle is travelling before it is brought to rest by collisions with molecules of the medium through which it is moving. At atmospheric pressure an atom will travel about 0·1 mm. through air. Take, for example, the case of radium B formed from radium A. The velocity of the α particle from RaA is $1{\cdot}77\times10^9$ cms. per second, and since the α particle is a charged atom of helium, its atomic weight is 4. The atomic weight of RaB is 214, so that from the laws of momentum the atom of RaB must be travelling at the rate of $3{\cdot}3\times10^7$ cms. per second immediately after the expulsion of the α particle. Now, it has been shown by Russ and Makower (*ibid.* 1909, 82) that the recoiling atoms travel considerable distances through a vacuum, and can be collected on a surface placed to receive them. In this way RaB may be completely separated from RaA, and can be obtained in a state of high purity. A more convenient way of effecting the separation was discovered independently by Hahn and Meitner (Verh. der Deutsch. Physik. Ges. 11, 3), who give a method of avoiding working *in vacuô*. To take the same example as above, if a plate coated with RaA is charged positively and a second negatively charged surface is brought near the first plate, the recoiling atoms of RaB are collected on the negative surface. Hahn and Meitner have in this way isolated several new products, amongst which may be mentioned thorium D and the product radium C″, which will be mentioned later. Later experiments by Russ and Makower and Makower and Evans have shown that a 'recoil-stream' of atoms of RaB is positively charged, and can be deflected when passing through an electric or magnetic field (Phil. Mag. 1910). The experiments show that the recoiling atoms move with a velocity of $3{\cdot}23\times10^7$ cms. per second, and each carry a unit charge of electricity. A rough determination of the atomic weight of RaB is also made which agrees with the value predicted by theory. More accurate measurements on the magnetic deflection of the recoil-stream have been made by Walmsley and Makower (Phil. Mag. 1915), and the case of the recoil of RaD from RaC has been investigated by Wood and Makower (Phil. Mag. 1915). The product RaC″ has been further studied by Fajans (Physikal. Zeitsch. 1911, 12), who shows that RaC″ is formed only in very small quantity from RaC. From recent experiments it appears that on breaking up RaC usually disintegrates with the production of radium D through the short-lived product RaC′, but occasionally through the product RaC″ instead. Another case of a side branch has been discovered by Antonoff, who finds that uranium can produce a product named UrY in small quantity as an alternative to UrX (Phil. Mag. 1911). This branch forms the starting-point of the actinium series through the product protactinium (Hahn and Meitner, Phys. Zeit. 1918, 19, 208; 1919, 20, 127; 1919, 20, 529; and Hahn, *ibid.* 1920, 21, 591).

§ (8) **Disintegration Series.** A general survey of the known radioactive elements and their connection with each other will now be given. No connection has yet been found between the thorium and uranium series of disintegration

products. Uranium and actinium are, however, related, as indicated in Table II. (Soddy and Cranston, Proc. Roy. Soc. 1918). The element polonium has been shown to be a disintegration product of radium and to be identical with RaF. A definite relation has also been established between uranium and radium. Just as is the case with all radioactive elements, radium is constantly disintegrating. It can easily be calculated that the half-value period of radium is about 2000 years, so that it is difficult to understand how this element can have persisted through geological ages in minerals, unless it is being supplied from some source. It was suggested by Rutherford and Soddy that the supply was derived from uranium, and this has since been proved to be the case by the experiments of McCoy (Ber. 1904, 37), Boltwood (Phil. Mag. 1905), and Strutt (Proc. Roy. Soc. 1905, &c.), who have shown that the ratio of the amount of radium to that of uranium in old minerals is nearly always constant. This is exactly what would be expected if radium were produced from uranium and sufficient time had elapsed for radioactive equilibrium to be set up. Experiment for a long time failed to reveal the production of radium from uranium, although the transformation should be proceeding sufficiently rapidly to be detected. Soddy has shown that not more than $\frac{1}{10000}$ of the amount of radium to be expected is formed from a solution of uranium (Phil. Mag. 1905). The explanation of this discrepancy has been given by Boltwood, who has isolated a product of very long period between uranium and radium, named by him *ionium* (*q.v.*) (Amer. J. Sci. 1906, 1907, 1908).

In the thorium series, some very active products have been separated by Hahn, who has shown that thorium is immediately followed by three products besides ThX before the emanation is reached. These have been called mesothorium 1 and 2 and radiothorium respectively. Hahn has prepared specimens of mesothorium of activity nearly equal to that of radium (Proc. Roy. Soc. 1905, [A] 76, 115; Ber. 1907, 40, 1462; Phys. Zeit. 1907, 8, 277; *ibid.* 1908, 9, 246). A complete list of the known radioactive elements is given in the tables, together with important data relating to them. In the case of products which emit α-rays the ranges in air at atmospheric pressure and 0° are given. The analogy between the three emanations and the products immediately following them is very striking.

In Table I. lead is given as the last disintegration product of uranium immediately following RaF. The indirect evidence upon which this conclusion is based is of two kinds. In the first place the work of Boltwood has shown that lead always occurs in radioactive minerals in such amount as is to be expected if it has been formed from uranium (Amer. J. Sci. 1905, 1907). The conclusion drawn by Boltwood is also supported by the following theoretical consideration. Polonium (RaF) is formed from radium as the result of a number of transformations involving the loss of seven α particles. Now, since the atomic weight of uranium is 238, and that of each α particle is 4, the atomic weight of polonium should be 210. Now, polonium emits α particles, so that the atomic weight of the next product should be 206, a value which is very close to the known atomic weight of lead.

TABLE I.

Uranium Series.			Thorium Series.			Actinium Series.		
Product.	Period.	Radiation and Range at N.T.P.	Product.	Period.	Radiation and Range at N.T.P.	Product.	Period.	Radiation and Range at N.T.P.
Uranium 1	5×10^9 years	α (2·53 cm.)	Thorium	$1{\cdot}3\times10^{10}$ yrs.	α (2·75 cm.)	Protactinium	$1{\cdot}2\times10^4$ yrs.	α (3·48 cm.)
Uranium X_1	24·6 days	β, γ	Mesothorium 1	6·7 years	—	Actinium	20 years	—
Uranium X_2	1·17 min.	β, γ	Mesothorium 2	6·2 hours	β, γ	Radioactinium	19·5 days	α (4·43 cm.), β
Uranium 2 (Uranium Y)	2×10^6 years	α (2·91 cm.)	Radiothorium	1·9 years	α (3·81 cm.)	Actinium X	11·6 days	α (4·14 cm.), β
	25·5 hours	β	Thorium X	3·7 days	α (4·13 cm.), β	Ac Emanation	3·9 secs.	α (5·49 cm.)
Ionium	2×10^5 years	α (3·03 cm.)	Th Emanation	54·5 secs.	α (4·80 cm.)	AcA	0·002 sec.	α (6·24 cm.)
Radium	2000 years	α (3·21 cm.), β	ThA	0·14 sec.	α (5·39 cm.)	AcB	36·3 mins.	β, γ
Ra Emanation	3·85 days	α (3·91 cm.)	ThB	10·6 hours	β, γ	AcC	2·15 mins.	α (5·22 cm.)
RaA	3·0 mins.	α (4·48 cm.)	ThC	60·8 mins.	α (4·54 cm.), β	(AcC′)	very short	α (6·4 cm.)
RaB	26·7 mins.	β, γ	(ThC′)	very short	α (8·17 cm.)	AcC″	4·71 mins.	β, γ
RaC	19·5 mins.	β, γ	ThC″	3·1 mins.	β, γ	Lead	—	—
RaC′ (RaC″)	very short	α (6·61 cm.)	Lead	—	—			
RaD	1·4 min.	β						
RaE	16·5 years	β, γ						
RaF (Polonium)	5·0 days	β, γ						
Lead	136 days	α (3·72 cm.)						
	—	—						

§ (9) **Periodic System and the Radioactive Elements.** The question of the positions of the radio-elements in Mendeléeff's periodic system has recently received much attention, resulting in

interesting and important new results. Fajans (Phys. Zeitsch. 1913) first drew attention to the fact that in transformations involving the emission of β-rays the resulting product is more electronegative than the parent substance. The reverse is true with α-ray transformations, and Soddy (Chemistry of Radio-elements, 30) showed that in such a case the atom changes from a group of even number in the periodic system to the next lower even group. A generalisation of these results has been given independently by Russell (Chem. News, 1913) and by Fajans (Ber. and Phys. Zeitsch. 1913), which may be stated thus: In an α-ray transformation the product falls into a group *two* places lower than that to which the parent substance belongs; whereas in a α-ray transformation the product falls into a group *one* place higher than the parent substance in the periodic system. The resultant grouping of the radio-elements is shown in Table II. It will be seen that according to this

TABLE II.—*Periodic Arrangement of Radio-elements.*

Group in Periodic System.	VII. A	VI. A	V. A	IV. A	III. A	II. A	I. A	0	VII. B	VI. B	V. B	IV. B	III. B	II. B	I. B
Element of Highest Atomic Weight.	Mn	Ur	Ta	Th	La	Ra	Cs	Xe	I	Te	Bi	Pb	Th	Hg	Au
Uranium-Radium Series.	α 8%	Ur1 —α 92%→		Ur X_1											
		↙β Ur X_2													
		Ur2 —β→		Io —	α →	Ra —	α →	Ra Em	α →	Ra A	α →	Ra B			
											↙β	Ra C α →	RaC″		
				Ur Y						↙					
			↙β *Ur Z* →		*Act*					RaC′	α →	Ra D			
										↙		↙β			
											Ra E				
										↙					
										Ra F	β →	Pb			
Thorium Series.				Th — α →	Meso Th_1										
					↙β										
					Meso Th_2										
					↙β										
				Radio-Th	α →	Th X	α →	Th Em	α →	Th A	α →	Th B			
											↙β				
											Th C	→	Th D		
												↙			
												Pb			
Actinium Series.					Act										
					↙										
				Radio-Act	α →	Act X	α →	Act Em	α →	Act A	α →	Act B			
											↙β				
											Act C	α →	Act D		
										↙		↙β			
										Act C′	→	Pb			

scheme several different products fall into the same spaces in the periodic system. Such products are known as *isotopes*, and are so similar that they are inseparable by any chemical means; their spectra appear also to be identical. It will thus be seen that atoms of different atomic weight exist, having identical chemical properties. As an example, RaB, RaD, ThB, and AcB are isotopes in group IV. B, and are therefore inseparable from one another and from lead.

Reference to Table II. shows that the end products of the uranium-radium, thorium, and actinium series are all in group IV. B, suggesting

that the final product of each series is lead. The atomic weight of lead formed in these three ways should, however, be different, that for lead from uranium being 206, and that from thorium 208. Evidence that this is so has been given by Soddy and Hyman (Chem. Soc. 1914), by Soddy (Nature, 1917), and by Hönigschmid (Zeit. Elektrochem. 1917, 23, 161; Phys. Zeit. 1917, 18, 114). The existence of isotopes amongst the non-radioactive elements has been established by Aston (Phil. Mag. 1919, 1920, &c.).

§ (10) **Emission of Heat by Radioactive Bodies.** Curie and Laborde were the first to show that radium is always at a temperature above surrounding bodies (Compt. rend. 1904, 136). Many experimenters have since measured the heat emitted by radium, and the determination by Schweidler and Hess gives the value 118 calories per hour per gram of radium (Wien. Ber. 1908). Rutherford and Barnes have made a detailed examination of the heat emitted by the products of radium separately, and have shown that the heat generated is derived mainly from the energy of the α particles emitted (Phil. Mag. 1904). In a later series of experiments Rutherford and Robinson have investigated the problem in much greater detail and have determined the heating effect of the α-, β-, and γ-rays from each product (*ibid.* 1913). The β- and γ-rays seem to be responsible only for a very small part of the heat evolved. Measurements on other products have confirmed the view that the heat developed in radioactive changes is approximately proportional to the energy of the α particles. It will be noticed that the emission of heat by radium is very large, being sufficient to melt its own weight of ice in 40 minutes. This evolution of energy during radioactive changes may be taken as indicative of the enormous stores of energy which must be contained within the atoms.

The figures in Table I. show a certain relation between the period p of a substance emitting α-rays, and the range r of those rays. Rutherford was the first to draw attention to the existence of such a relation, pointing out that in general p was large when r was small (Phil. Mag. 1907). Geiger and Nuttall have made fresh determinations of several ranges which had previously been somewhat uncertain (*ibid.* 1911); the latest and most accurate determinations are by Geiger (Zeit. f. Physik. 1921), and these have been used in the construction of the table. They have taken the opportunity to re-examine the relation between p and r and find that for the radium series, and also for the actinium series, p and r are connected by the relation $rp^a=b$. Here a and b are constant, the former being the same for both series. From this relation it can be shown that the life of a substance emitting rays of short range, say 1 cm., would be so long, and therefore its transformation so slow, that its activity would be beyond the limits of detection by present methods.

W. M.

(B) *Radiations Emitted by Radioactive Substances.*

§ (1) **General.** This section deals with the phenomena attending the passage of α-, β-, and γ rays through matter.

It is convenient to divide them into two parts: (i.) those referring to the action upon the rays; (ii.) those referring to the action upon the matter.

Further subdivision is convenient in respect to the phenomena of part (i.). The experience of an α-, a β-, or a γ-ray as it flies across an atom may be considered under three heads: (*a*) loss of energy, (*b*) deflection, (*c*) transformation or replacement. The α particle's experiences are mostly under (*a*): it is only slightly liable to scattering (*b*), and not at all to change of form (*c*). The β particle is very liable to deflection, which often makes its loss of energy difficult to detect, and it is liable to transformation into a γ-ray—the X-ray may be included as a form of γ-ray—especially if its velocity is not more than about one-third of that of light. The γ-ray (or X-ray) appears to suffer no loss of energy, and is somewhat liable to scattering; the most interesting and important event in its history is the transformation of its energy into that of a β-ray.

The most obvious of the phenomena to be included under (ii.) are heating, photographic action, phosphorescence, ionisation. The last three are used as indicators of the action of the rays.

In all cases known the phenomena of part (i.) are independent of physical and chemical conditions. For example, the probable loss of energy of an α particle in going through a definite small volume containing an atom does not depend on whether the atom is part of a hot body or of a cold body, of a solid or of a gas, of a simple molecule or of a complex one.

On the other hand, some of the phenomena of part (ii.) are not quite so simple. The number of ions which can be extracted from a gas after an α particle has passed through it depends somewhat upon molecular association.

The α- and β-rays are really projectiles of very small mass, but of enormous speed. It would appear that the γ-ray (and the X-ray which has similar properties) may also be reasonably and usefully considered as in some ways analogous to a projectile. In the case of any of these forms of radiation small entities, quanta, or corpuscles are hurled against matter with relative speeds far exceeding those of the thermal agitation of a gas at any temperature yet realised. The results are peculiar, as might be expected. In particular the atoms are no longer impenetrable, but are traversed with the utmost freedom; and the actions and reactions between the projectiles and the atoms are of the greatest interest, affording glimpses of the atomic constitution from an entirely new standpoint.

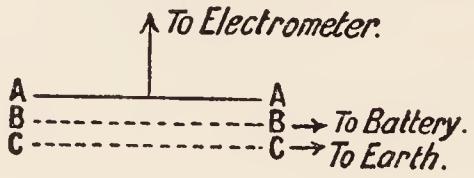
We now take the three radiations in turn.

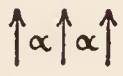
§ (2) **The α-ray.** (i) *Nature of α-ray.*—The almost universal presence of helium in radioactive minerals early suggested the nature of the α particle. A simple verification has been given by Rutherford and Royds (Phil. Mag. 1909). Radium emanation is enclosed in a glass tube with very thin walls, through which α radiations can pass. Outside the tube is an evacuated space, which shows no trace of the helium spectrum when sparked through immediately after the preparation of the tube. In a few days, however, the helium lines are strongly

shown. In control experiments, when the inner tube is empty, and even when it is filled with helium, there is no such effect. It is clear that the emanation has shot helium through the glass.

(ii) *Velocity of α particle.*—Rutherford has determined the velocity of the α particle and the ratio of its charge to its mass by observing the effect of electric and magnetic fields upon its flight (Phil. Mag. 1906). The latter quantity he finds to be nearly 5×10^3, which shows that the α particle being a helium atom must carry twice the unit charge. The velocity will be considered later.

(iii) *Range of α particle.*—Since the α particle is very little scattered by the matter through which it passes, its path is almost exactly a straight line. It spends its energy as it goes, and, having spent it, comes to comparative rest at a certain distance from the starting-point, which distance is called the range. The range varies with the initial speed and with the nature and density of the gas traversed. It was first found, in the case of





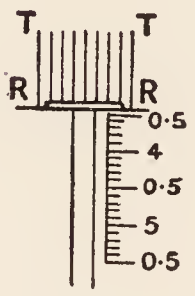


Fig. 1.

the α-rays of radium, by means of apparatus represented in the diagram (Fig. 1). A very thin layer of radium is placed on a plate RR. The α-rays stream upwards in all directions, but only those which proceed almost vertically succeed in passing through the set of tubes, TT. These are made of thin copper foil 1 cm. long and 2 mm. wide; the bundle contains about 150 of them. The α-rays which strike the walls of the tubes are embedded there. The rest stream upwards, ionising the gas; if they reach the gauze BB, and enter the ionisation chamber between BB and AA, then ionisation occurs in the chamber also, and is detected in the usual way. The lower gauze, CC, is connected with the earth, and the field between BB and CC protects the ionisation chamber from the intrusion of ions from below. The radium is gradually raised towards the chamber and the current measured for different positions; the 'ionisation curve' is thus obtained (Fig. 2) (Bragg and Kleeman, Phil. Mag. 1905). This curve is interpreted as follows. The small readings above A are due to the action of β- and γ-rays. The sudden setting in of current at A, 7·14 cm. from the origin, implies that this is the furthest point of penetration of the α-rays. This distance

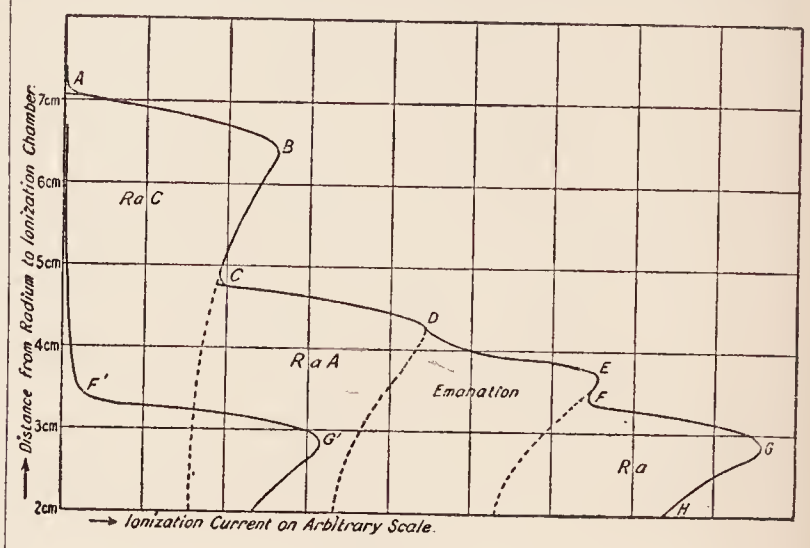


Fig. 2.

is termed the range of the α particle in question. It is 7·14 cm. in air at a pressure of 76 cm. and a temperature of 20°. The range at any other pressure (P) and absolute temperature (T) is $7\cdot14\times(76/P)\times(T/293)$. The slope, AB, is due to the fact that all the α-rays do not reach quite the same distance from the radium; the turn at B shows that at 6·5 cm. all the rays—of this stream—now make their way into the chamber. The gradual bend back, BC, implies that the α particle is more effective as an ioniser as it slows down. The sudden break out again at C (4·84 cm.) shows that the chamber is now within range of a second stream of α particles of shorter range than the first, and the portions DE and FG show that there are yet two other streams of still less range. When the radium layer is taken out, heated to a bright red heat and replaced in the apparatus, the middle parts of the curve CD and DE are found to have disappeared, and in an hour or so the top part AB has disappeared also, the curve therefore reducing to F′G′. Now it is known that the heating has driven off the emanation, and the RaA must have quickly followed the source of its existence. We conclude that the α-stream of least range (3·50 cm.) is due to radium itself, and that of greatest range is due to RaC. By separate experiment it is shown that the range of the α particle of RaA is the longer of the two intermediate quantities, 4·84; and that the other, 4·23, belongs to the emanation. Each of the radioactive substances has thus its own range; and further, since the four steps of the curve are of exactly the same width, the rate of emission of particles from each product is the same, which is in agreement with Rutherford and Soddy's theory of radioactive change.

The ranges of the α particles of other substances can generally be found in similar fashion: difficulty arises only in the case of those which radiate weakly. In such cases the ranges have been determined by a special method devised by Geiger and Nuttall (Phil. Mag. 1911), who give a complete list of the ranges from different products.

(iv) *Stopping power of metal foils.*—When a thin sheet of uniform material is placed over the tubes TT, so that the α particles must go through it, each particle loses a definite amount of its range, and the ionisation curve is

correspondingly lowered (Fig. 3). The exact resemblance of the new curve to the old shows that the particles have lost neither in number nor in direction, so that they must have passed through all the atoms they have met in going through the sheet; the helium atom has freely penetrated the silver atoms. On comparing the effects of sheets of different materials the remarkable result appears that the masses of equivalent sheets (per cm.^{2}) are proportional to the square roots of the atomic weights of the substances of which they are composed. We may define the 'stopping power' of an atom as the probable loss of range which an α particle experiences in passing through a small volume containing only that atom, compared with the similar probable loss when some standard atom is substituted. We may conveniently take an imaginary air atom as standard (at.wt.$=14{\cdot}4$): the table on the next page gives the values of the stopping powers (s) of some molecules relative to the imaginary air molecule. The stopping power of a molecule is the sum of the stopping powers of the atoms of which it is composed;

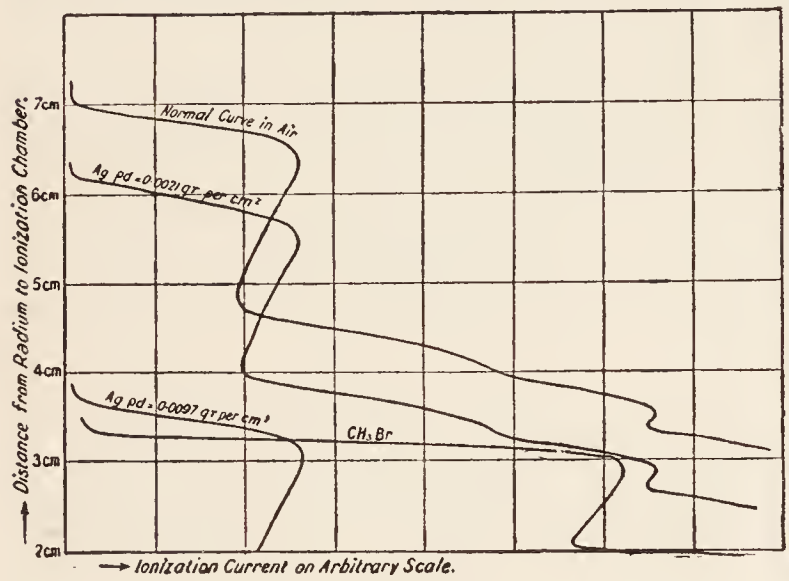


FIG. 3.

e.g. the stopping power of N_2O is to that of C_6H_6 in the proportion $2\sqrt{14}+\sqrt{16}$ to $6\sqrt{12}+6\sqrt{1}$ or 0·43. Experiment (*see* table below) gives 0·44.

The stopping power of a gas is found by comparing the range of the α particle in the gas with the range in the air. An atom or molecule has the same stopping power, no matter whether it is part of a solid or of a gas.

(v) *α-ray tracks.*—The α particle is, as already mentioned, liable to deflection in passing through the atom. But the effect is small and unimportant except when its velocity becomes small. The remarkably rectilinear path of the particle has been beautifully illustrated by C. T. R. Wilson, Proc. Roy. Soc. 85, 285, and 87, 277. A chamber containing damp air is for a moment subjected to the action of the rays, and is immediately afterwards chilled by a sudden expansion of the air. Fog settles on the ions left along the track of the particle; Fig. 4 is a reproduction of a photograph of the event. The sharp lines belong to α particles which went by the instant before the expansion; the more diffused lines to those that were shot out a little earlier so that the ions have had time to spread somewhat.

Similar results have been obtained by observing the effects of α particles as they pass through a photographic film. If an α particle is projected tangentially to a photographic film, after development the film shows definite trails

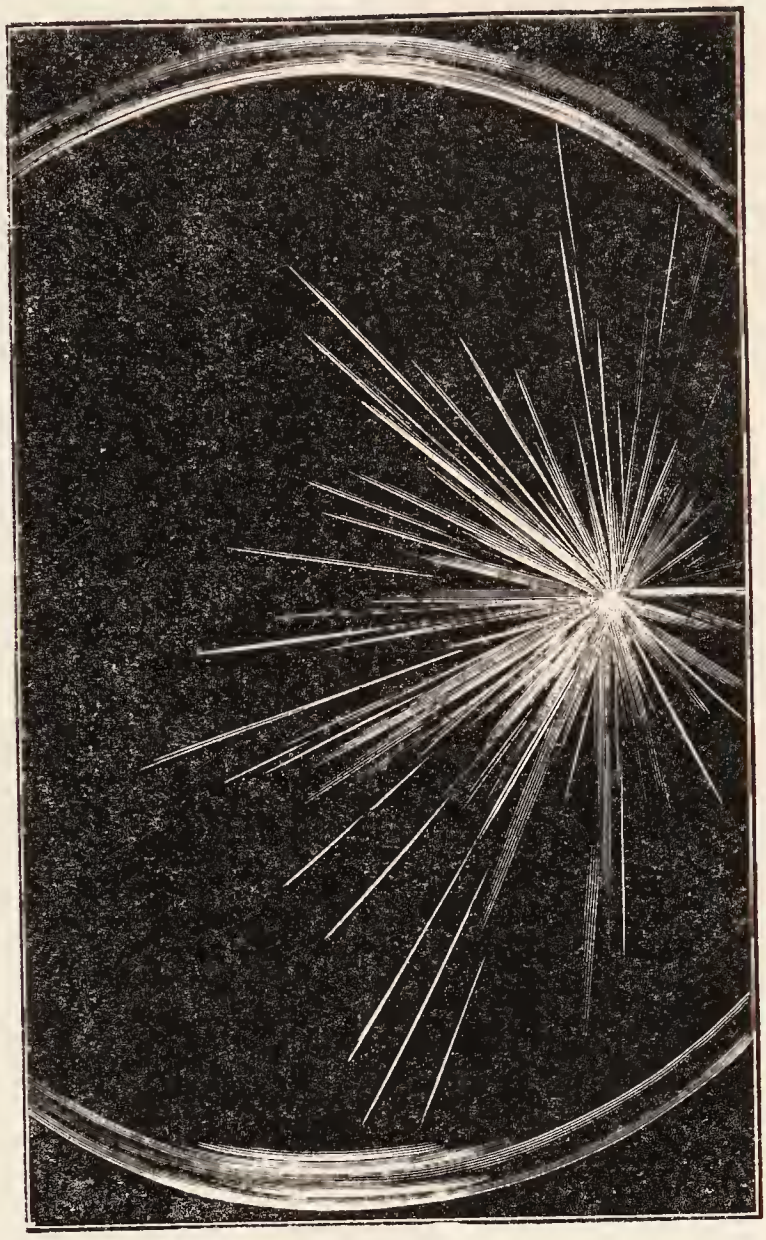


FIG. 4.

of grains of silver halide which can readily be distinguished under the microscope. Microphotographs of this kind have been made by Walmsley and Makower (Phys. Soc. 1914), and later Kinoshita and Ikeuti (Phil. Mag. 1915), published very beautiful microphotographs illustrating very strikingly the phenomena accompanying the passage of α particles through matter.

(vi) *Scattering of α-rays.*—The scattering of the particle has been investigated by Rutherford and Geiger by the 'scintillation' method. When a stream of particles strikes a phosphorescent screen, such as zinc sulphide, the blow of every particle causes a momentary sparkle, and the numbers falling on any particular portion of the

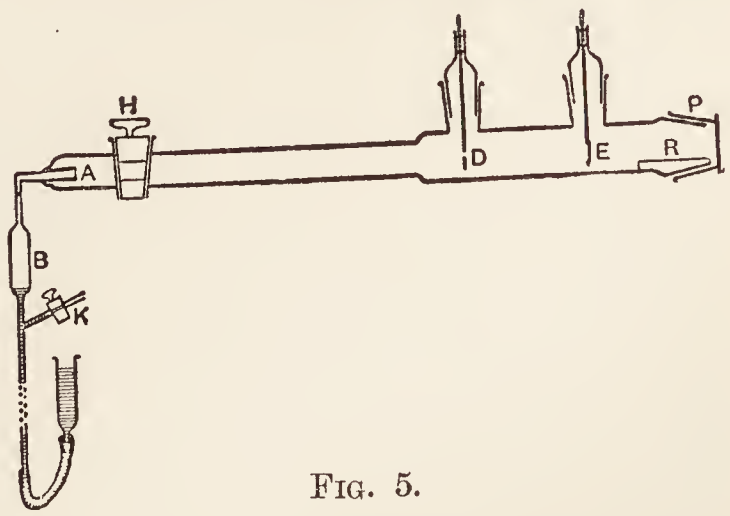


FIG. 5.

screen can be counted under the microscope. The apparatus is shown in Fig. 5 (Geiger, Proc.

Roy. Soc. 83, 493). Some emanation is for a time compressed in the conical opening of the tube at A, and is then withdrawn. The active deposit which it leaves behind shoots α particles down the exhausted tube through small openings at D and E, and these fall on the phosphorescent screen at S. Screens can be put at E or on R, and the consequent scattering is then observed. It is very small. When, for example, the α particle passes through 20 gold leaves weighing about 3·5 mmg. per cm.^{2} the most probable angle of deflection is only 1° 40′. Comparing different substances, the most probable angle of deflection is proportional to the atomic weight. The scattering also depends on the velocity, increasing rapidly as the particle slows down, and being to a first approximation inversely proportional to the cube of the velocity. Near the end of its path, therefore, the particle may experience some very violent deflections; finally, it settles down to the usual movements of a gas atom.

(vii) *Rate of emission of α particles from radium.*—By the scintillation method, and by a method of intensifying the ionisation effect of the single α particle, Rutherford and Geiger have determined the rate at which radium emits α particles. Having found also the total charge of electricity conveyed by these particles, they have determined the charge carried by each one (Proc. Roy. Soc. 81, 141, 162). They give the following results:—

Charge (e) carried by the hydrogen atom in electrolysis$=4{\cdot}65\times10^{-10}$ E.S. unit.

Charge carried by the α particle$=9{\cdot}3\times10^{-10}$ E.S. unit.

The value of Ne, where N is the number of hydrogen atoms in 1 grm. of hydrogen, being known from electrolysis, it is readily found that $N=6{\cdot}2\times10^{23}$, that the mass of the hydrogen atom is $1{\cdot}61\times10^{-24}$ grms., and that the number of molecules per c.c. of any gas at standard pressure and temperature is $2{\cdot}72\times10^{19}$.

(viii) *Relation between range and velocity of α particles.*—Rutherford and Hahn have measured the velocities of the α particles of various substances (Phil. Mag. 1906), and Geiger has shown that the initial velocity is connected with the range by the formula $v^3=a\mathrm{R}$ (Proc. Roy. Soc. 83, 505). A very accurate determination has been made by Rutherford and Robinson (Phil. Mag. 1914) of the electric and magnetic deflections of the α particles from RaC. They deduce the values $\frac{e}{m}=4823$ E.M. units and $v=1{\cdot}922\times10^9$ cm. per sec. The velocities of the α particles from other products can be calculated from their known ranges by the application of Geiger's formula.

In order to explain the deflection of the α particle by the atom, it is necessary, according to Rutherford (Phil. Mag. 1911), to suppose that each atom possesses a nucleus of electrical charge ne, where e is the unitary electrical charge and n is a number of the order of half the atomic weight, and proportional to that weight. For instance, if n be set equal to 100, the scatterings of the α particles observed by Geiger in the case of gold are in very good accordance with calculations based on this theory. On the vast majority of occasions, when an α particle goes through an atom it does not go near enough to the central charge to suffer serious deflection. When a stream of α particles is hurled against a gold plate, only one in each eight thousand is returned. It will be seen that the scattering of the β particles is also explained by Rutherford's hypothesis. The theory has been developed by Bohn (Phil. Mag. Oct. 1915), who has investigated in great detail the decrease in velocity to be expected when α and β particles pass through matter.

(ix) *Ionisation produced by α particle.*—Of the effects which the α particle exerts upon the matter which it traverses the most easily investigated is the ionisation. It is curious that molecular association is not quite without influence upon the total ionisation which a given α particle produces, although it does not count in the calculation of the energy which the particle spends. The total ionisation is greater ('k' times greater) in most gases than in air. We may define a quantity called the molecular ionisation, which will represent the probable ionisation produced when an α particle crosses a given volume containing the molecule in question. This is obtained by multiplying k by s, the stopping power, since the greater the latter quantity the fewer the molecules that contribute to the total ionisation. The molecular ionisation is not quite an additive quantity. It is roughly proportional to the volume of the molecule. A few values of these constants are given as illustrations:—

TABLE I.

	k.	s.	ks.
Air . .	1·00	1·00	1·00
CO_2 . .	1·03	1·50	1·55
C_2H_2 . .	1·26	1·118	1·40
C_2H_4 . .	1·22	1·32	1·61
C_2H_6 . .	1·30	1·51	1·96
CH_4 . .	1·17	0·86	1·005
H_2 . .	1·00	0·24	0·24
He . .	—	0·201	0·22
Ar . .	—	0·95	1·24

For the values of k and s in other gases, *see* Bragg (Phil. Mag. 1907), Metcalfe (*ibid.* 1909), Taylor (*ibid.* 1911).

§ (3) **The β-ray.** (i) *Velocity of β particle.*—The direction of deflection of the β-ray in a magnetic field shows at once that it is a negatively charged body. Measurements of the deflections in crossed electric and magnetic fields (*e.g.* those of Kaufmann, Annalen Physik. 1906, [iv.] 19, 487) give the velocity (v) and the ratio of charge to mass (e/m). The latter quantity is the same as that of the electron, unless the speed is very great, and this practically identifies the β-ray with the electron. The ratio is found to diminish as the velocity approaches that of light. The diminution is such as would be expected, on electro-magnetic theory, if the mass of the electron were wholly electro-magnetic. When $v=0{\cdot}94\mathrm{V}$, where V= the velocity of light, $e/m=0{\cdot}63\times10^7$ E.M.U.; when $v=0{\cdot}59\mathrm{V}$, $e/m=1{\cdot}68\times10^7$. The β-rays of radium vary considerably in speed, some moving with a velocity little less than that of light.

In its movement through matter the β particle is much more liable to deflection

than the α particle, and a stream of particles directed against a material screen loses rather by deflection of individuals than by general slowing down. The degree of penetration depends very largely on the speed. The β-ray of radium can sometimes traverse a few metres of air, whilst ' cathode rays ' of one-third the speed are nearly all absorbed in two or three millimetres.

(ii) *Magnetic deflection of β-rays.*—The movements and penetrations of β-rays are beautifully shown in some early experiments by Becquerel, which are illustrated in the accompanying figures. Fig. 6 is diagrammatic, and shows how

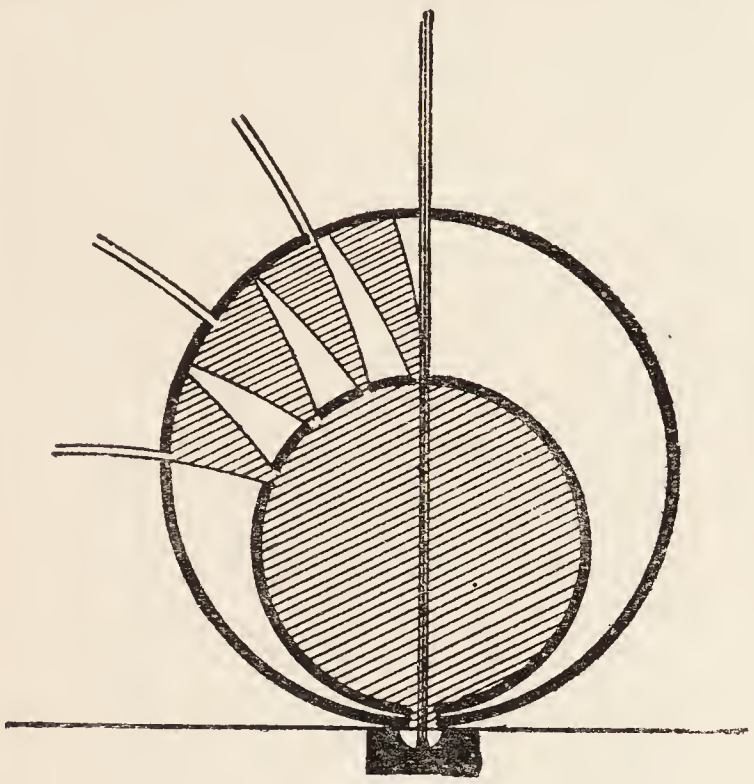


Fig. 6.

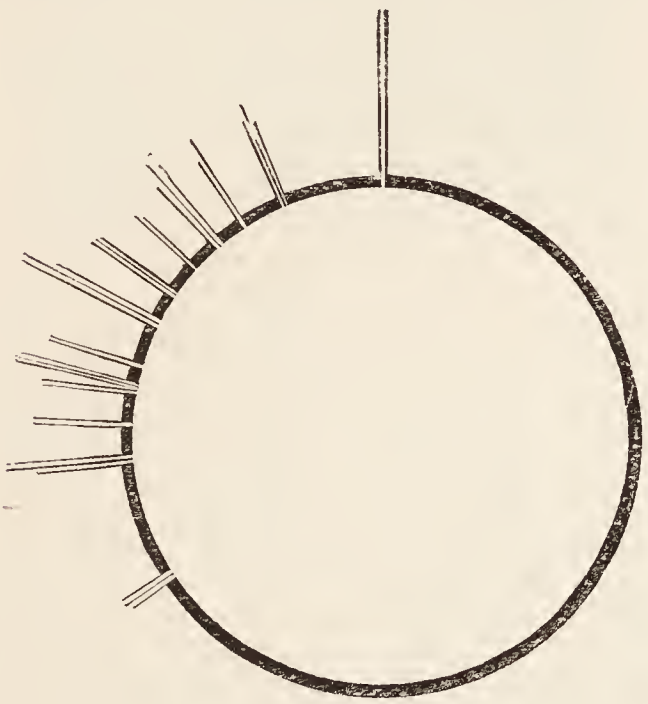


Fig. 7.

the β-rays from a small quantity of radium are swung round in circles by a magnetic field through openings in certain screens. The rays skirt a photographic plate in the plane of the paper, and leave records of their paths. Fig. 7 shows what happens when a sheet of Al 0·1 mm. thick is placed over all the holes in the outer screen, so that the β-rays have to go through it. It will be observed that the faster β-rays at least —those moving in the circles of least curvature —retain their direction after passing through the layer. The scattering may also be observed by measuring the ionisation which the deflected rays produce in chambers suitably placed. When a stream is directed against a plate, the number of rays swung round so far as to re-emerge on the side on which the stream is incident increases rapidly with the atomic weight of the substance of the plate (McClelland, Roy. Dublin Soc. Trans. 1905 *et seq.*). The central charge or nucleus which Rutherford found necessary to explain the deflection of the α particle gives a satisfactory explanation of the deflections of the β particles also.

From Becquerel's experiment and from many others, such as, for example, those of Madsen (Phil. Mag. 1909), it appears that a penetrating β-ray must generally traverse thin sheets of metal without any serious deflection, and the few which have been turned aside out of the main stream have only been deflected once. Thus observations of the distribution of the scattered rays give information as to the probable result of the encounter of a single electron with a single atom. Information of this kind is most desirable as helping to a knowledge of atomic constitution.

(iii) *Loss of energy of β particle in traversing matter.*—The β particle suffers a loss in speed in going through matter, but for a long time the loss was unobserved; it is difficult to measure with certainty because the scattering effects mask it. W. Wilson found (Proc. Roy. Soc. 84, 141) that the energy of a β-ray fell off in proportion to the amount of matter penetrated. An initial velocity of $2{\cdot}85\times10^{10}$ cm./sec. was reduced to $2{\cdot}80\times10^{10}$ by a screen of aluminium 0·5 mm. thick, to $2{\cdot}70\times10^{10}$ by a screen 1·0 mm. thick, and to $2{\cdot}25\times10^{10}$ by a screen 1·7 mm. thick. The scattering of the β particle increases very fast as its speed decays, and the power of penetrating material is affected more by chance of scattering than by loss of velocity. The β particles of the highest speed named above are seven times as penetrating as those of the lowest, chiefly on account of differences in the liability to scattering. The loss of velocity depends on the nature of the matter in somewhat the same fashion as in the case of the α-rays. The loss in passing through an atom is proprotional to $w^{2/3}$, where w is the atomic weight; in the case of the α particle, it is proportional to $w^{1/2}$, as already said. The whole of this may be compressed into the statement that in a substance of small atomic weight like aluminium a particle projected with given velocity reaches a greater distance from the origin (measured by mass penetrated) than it does in a substance of large atomic weight like platinum. But it really pursues a longer path in the latter (again measured by amount of matter traversed), only the path is much more broken and irregular.

(iv) *β-ray spectra.*—Rutherford has shown (Phil. Mag. Oct. 1912) that the heterogeneous β-radiation from a substance like RaC consist of a group of homogeneous β-radiations. The energy of each member of a group is characteristic of that group. The difference between the energies of any two groups is closely connected with the energy required to excite the X- (or γ-) radiation characteristic of the radioactive substance, a quantity which is found by extrapolation

from X-ray measurements with substances of lower atomic weight. This work also suggests the interchangeability of the energy of the β- and the X- or γ-ray, with the additional hypothesis that in the process of expulsion from the radioactive atom, one β-ray may give rise to more than one γ-ray, and *vice versâ*.

The problem of the distribution of the velocities of the β-rays from radioactive products has been carefully studied, and 'spectra' of the rays from different products have been obtained by examining the radiations in a magnetic field. The early experiments of Hahn, Baeyer and Meitner on the subject were improved by Danysz (Comp. rend. 1911) in the case of RaB and RaC, and a most exhaustive examination of the radiations from these products was made by Rutherford and Robinson by a special method (Phil. Mag. 1913). The results obtained are shown in Fig. 8, which illustrates the extreme complexity of the 'magnetic spectra'; some of the principal lines are marked with letters. The relation between the groups of β- and γ-radiation emitted by radioactive products is of the greatest theoretical importance and has been discussed by Rutherford (*ibid.* 1914).

(v) *Ionisation of different gases by β-rays.*— The ionisation produced in a gas by a stream of β-rays varies with the nature of the gas in much the same way as in the case of the α-rays (Kleeman, Proc. Roy. Soc. 79, 220). A few examples of molecular ionisations by α-, β-, and γ-rays are given side by side in the following table:—

TABLE II.

	α	β	γ
Air .	1·00	1·00	1·00
CO_2 .	1·59	1·60	1·58
C_2H_4O .	2·14	2·12	2·17
$CHCl_3$.	4·08	4·94	4·93
C_2H_5I .	4·00	5·90	6·47

Lastly, reference must be made to the chance of transformation of β-radiation. It is rarely observed in the case of the swift electrons emitted by radioactive substances; the only case known is that given by Gray (*ibid.* 85, 131), who found that the β-rays of RaE, which are very absorbable, produced γ-rays in substances on which they fell. In the case of the slower electrons of the vacuum tube, the effect is common enough, being in fact that on which the production of X-rays is based.

§ (4) **The γ-ray.** (i) *General properties.*— When γ-radiation, or X-radiation which differs from γ-radiation in degree, but not in kind, meets with matter there is a production of β-radiation. The energy of the γ-radiation is transformed into energy of the other. Since β-rays produce phosphorescence, ionisation, and photographic action, it may be assumed that these effects, when they accompany the passage of γ- or X-rays, are really the direct result of the β-rays, into which the γ- or X-rays are transformed. The laws of the transformation become the first object of investigation. It appears that in the first place the speed of the β-ray produced in this way increases with the penetrating power of the γ-ray; but it is independent of the intensity of the γ-ray and of the nature of the matter in which the transformation takes place. Secondly, the initial direction of motion of the β-ray is more or less a continuation of that of the γ-ray; more so, the more penetrating the latter ray, and the lighter the atom of the material. These facts

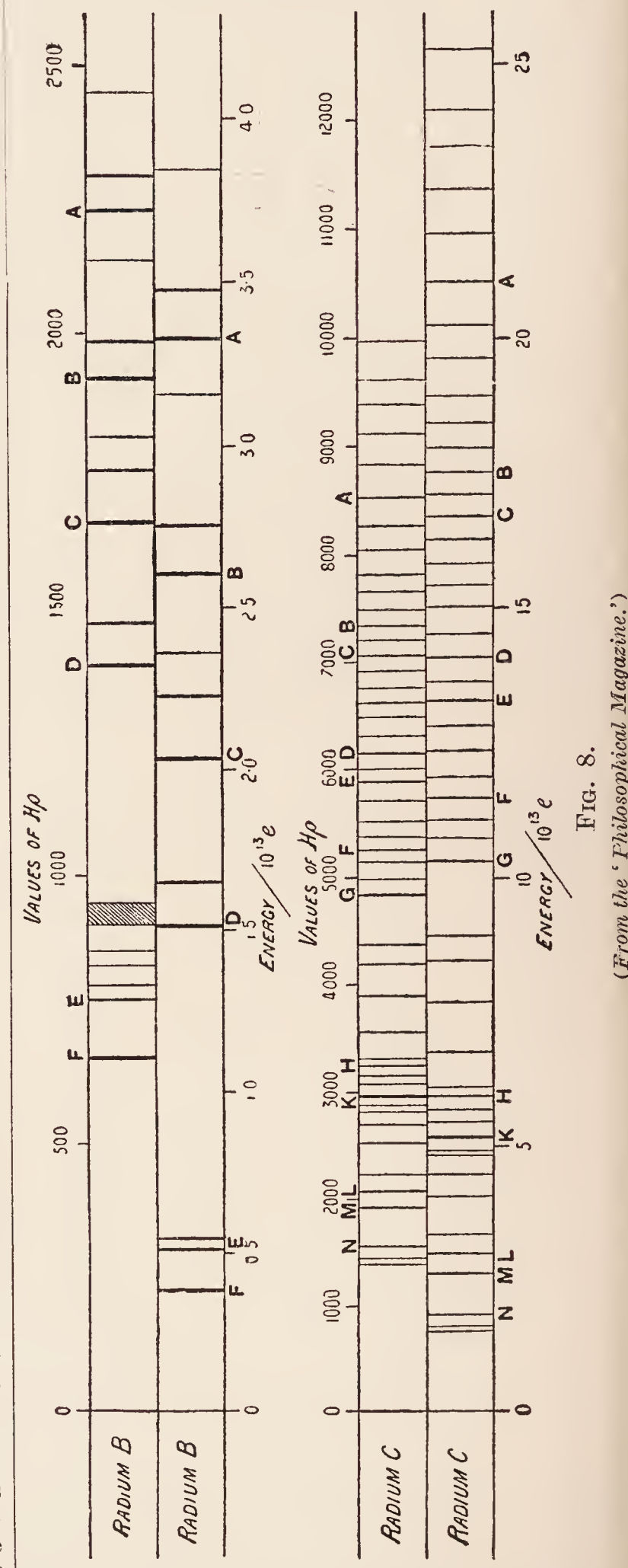


FIG. 8.
(From the 'Philosophical Magazine.')

suggest that the energy of each β-ray comes from the store of energy of one γ-ray, which in disappearing hands on energy and direction of motion to the electron which takes its place. The γ-ray energy must therefore be contained within a very small compass, and must keep its form and magnitude unchanged as it moves,

so that when the fatal encounter takes place in some atom the energy may be ready, undiminished, for transformation. It is a striking fact that the energy of the cathode ray, which produces the X-ray in the vacuum tube, is nearly the same as that of the cathode ray, which the X-ray produces, so far as present experiment can tell. It is at any rate not much greater. It may be concluded that the electron in the tube is there replaced by, or transformed into, an X-ray, and that the latter, if it succeeds in passing through the tube wall, is available for retransformation into a moving electron. The history of a γ-ray or X-ray, or of the energy carried by the ray, is therefore the history of an individual quantity of energy manifest now in one form, now in its alternative. As a γ-ray, the quantum must spend nothing as it goes through matter, since it has to carry its energy intact to the place of transformation; when it is in the β-ray form it is much liable to scattering, and liable also to diminution of energy, and interchanges proceed until all the energy has



Fig. 9.

been spent (Corpuscular theory of X- and γ-rays, Phil. Mag. 1910). An experiment of C. T. R. Wilson's illustrates this deduction; a fog is made to settle on the ions produced by the passage of X-rays through the air, and it will be observed (Fig. 9) that the ionisation lies on short irregular lines two or three millimetres long distributed in a promiscuous manner through the gas. These represent the tracks of the slow-moving β-rays into which X-rays are transformed by the atoms of the gas, and the effect realises anticipation very closely.

The energy of the X-ray must lie between that of the cathode ray which makes it and that of the cathode ray which it makes. The two extremes being not far apart and possibly identical, the energy of the X-ray is a sufficient and proper definition of its quality, and is a more fundamental basis of definition than the absorption in some material taken as standard. From analogy it may be supposed that the same applies to the γ-ray.

The deduction stated above, viz. that the X-ray produces no ionisation by direct action, but only through the agency of the β-ray, has been tested by Bragg and Porter (Proc. Roy. Soc. 85, 349), and found to be true within errors of experiment.

(ii) *Absorption of γ-rays.*—The 'absorption coefficient' of γ-rays in any substance is really a measure of the proportion that are converted into β-rays in crossing a given stratum of that substance. If this proportion is put equal to λdx, where dx is the product of the thickness of the stratum and its density, then for most substances λ is nearly 0·040 in the case of the γ-rays of radium and 0·047 in the case of the γ-rays of uranium. For lead and other substances of high atomic weight, it is a little larger (*see*, for example, Soddy and Russell, Phil. Mag. 1910).

(iii) *Scattering of γ-rays.*—The scattering of the γ-ray in its passage through matter has been examined by several workers, *e.g.* Madsen (Trans. Roy. Soc. of South Australia, 1908) and Florance (Phil. Mag. 1910). The latter states that if a stream of heterogeneous γ-rays from radium is scattered in passing through matter, that which is less penetrating is more scattered than that which is more penetrating. The analogous effect occurs in the case of the β-rays. Quite recently Ishino (Phil. Mag. 1917) has examined the scattering of γ- rays in relation to the absorption of the rays by matter.

(iv) *Nature of γ-rays.*—The nature of the γ-ray is still a matter of discussion. The æther pulse theory supposes the γ-ray to be the disturbance in the æther which must occur when a β-ray is discharged from the atom. Such a supposition links closely together γ-rays, X-rays, and light as variants of one form of radiation, and is based on the many points of resemblance between the three. Amongst resemblances of especial interest may be mentioned Barkla's discovery that X-rays can be polarised in a manner suggestive in some degree of the polarisation of light, and the remarkable experiments of Friedrich, Knipping, and Laue, which are best explained on the supposition that X-rays can be reflected in such planes within a crystal as are rich in atoms. The pulse theory is, however, unable to give a ready explanation of the interchangeability of X-ray and β-ray energy.

If the ionisation in a gas traversed by γ-rays is due to the β-rays produced by the γ-rays in the walls and in the gas, the 'ionisation of gases by γ-rays' is really an ionisation by β-rays. In the fourth column of Table II. some of the values found for the ionisation of gases by γ-rays are set out, and may be compared with the values in the third column (Kleeman, Proc. Roy. Soc. 79, 231).

W. H. B.

II. X-ray Spectroscopy.

§ (1) **Diffraction of X-rays.**—A great advance in the knowledge of the nature and properties of X-rays has taken place since the discovery of the diffraction of X-rays by crystals made by Laue in 1912. Atoms composing crystals are arranged on definite space lattices. Laue showed that if the distances between the atoms were of the right order of magnitude compared with the wavelength of the radiation, assuming that X-rays

are similar to light waves of very short wave-length, the crystal could be used as a three-dimensional grating to diffract X-rays. His analysis showed that when a beam of rays traverses a crystal, maxima of intensity should be found in certain directions, these directions depending upon the wave-length of the radiation and the distances between the atoms. Putting the theory to a practical test he, with Friedrich and Knipping (Sitzber. der K. Bayer, Akad. d. Wiss. June, 1912), obtained results which agreed with expectation. The experiments performed were of a simple character. A narrow pencil of X-rays was allowed to traverse a crystal of zinc blende, and then to fall on a photographic plate placed normally to the incident beam. The plate was developed after an exposure of several hours, and it was found that instead of a single black spot, as would be the case in the absence of the crystal, there was in addition a number of other spots of much smaller intensity. By tilting the crystal so that the rays traversed it along an axis of symmetry, the spots arranged

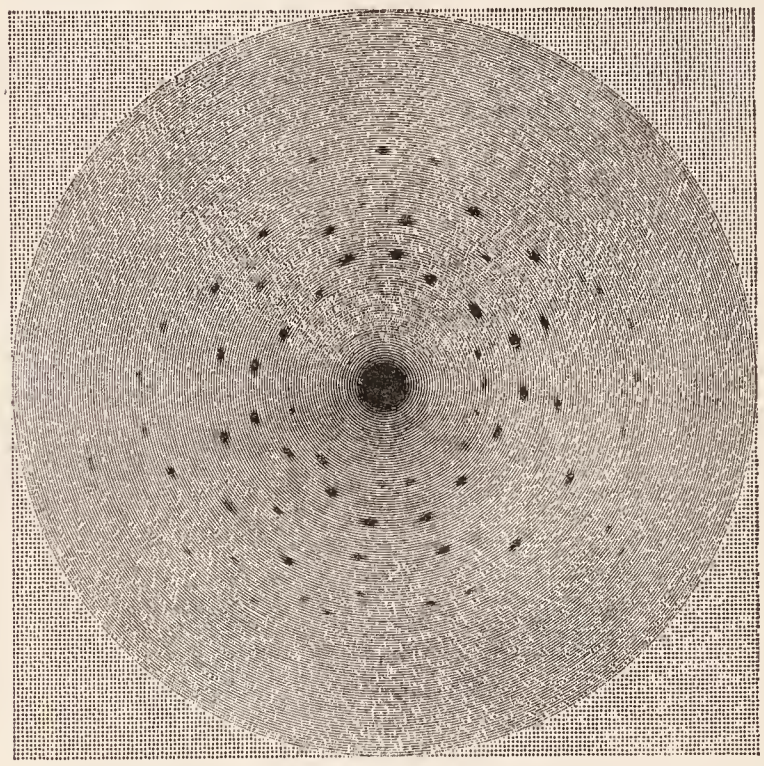


Fig. 10.

themselves symmetrically round the central spot. Fig. 10 is a photograph of the pattern obtained with a crystal of zinc blende placed so that one of its three principal cubic axes is in the direction of the incident beam.

Laue accounted for all the spots in the photograph by assuming the presence of only five wave-lengths in the incident radiation. If this assumption were correct, then some of the spots would disappear and others would appear in fresh positions as the crystal was gradually tilted. Experiment showed, however, that the same spot could be traced from one to another of a series of photographs taken with the crystal at slightly increasing angles with the incident beam. W. L. Bragg (Proc. Camb. Phil. Soc. 1912, 17) pointed out that this phenomenon could only be explained on the assumption that the incident radiation was made up of a continuous spectrum extending over a wide range of wave-lengths. The spots were found in positions corresponding to regular reflection from planes within the crystal that were rich in atoms, subject to the condition that the waves reflected from successive planes reinforced one another. On this view the rays should be regularly reflected from a surface such as that presented by the cleavage planes of a crystal. When a beam of X-rays was allowed to fall on the surface of a mica sheet at a glancing angle of about 10° a reflected spot was observed on the photographic plate. The variation of the angle of reflection with the angle of incidence left no doubt that the laws of reflection were obeyed. These experiments led to a simpler method of attacking the problem of the diffraction of X-rays by crystals.

Let the structure of a crystal be represented by a series of equidistant parallel planes $p_1 p_2 \ldots$. Suppose a beam of parallel rays of homogeneous radiation to fall on the surface at an angle θ. Consider the two rays AB and A′B′. These are in phase at A and A′; but after reflection at B and B′ respectively they will travel together in the direction BC, but will differ in phase at C by an amount represented by ND (*i.e.* the difference between B′B and B′N, where N is the foot of the perpendicular from B on A′B′). If d is the distance between consecutive planes then $ND = 2d \sin \theta$. If this phase difference is equal to a whole number of wave-lengths the waves will reinforce each other. When ND

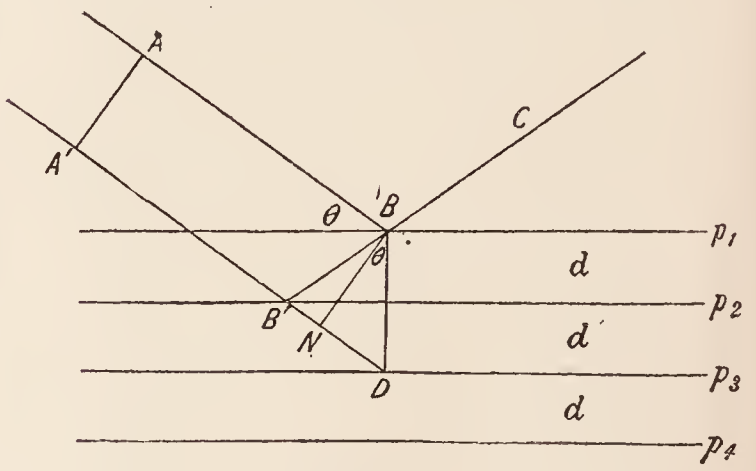


Fig. 11.

differs, however little, from a whole number of wave-lengths, then the waves reflected by the different planes destroy each other. In order, therefore, to obtain a maximum of intensity in any direction θ, the wave-length and the distance between consecutive planes of atoms must obey the relation $n\lambda = 2d \sin \theta$, where n is an integer. For another face of the crystal using the same radiation the condition would be $n\lambda = 2d' \sin \theta'$, and so on.

By measuring the angle at which reflection takes place in different faces of the crystal, using the same radiation in each case, the ratios of the spacings of the sets of planes parallel to those faces are directly found. On the other hand, by using the same face of a crystal, but altering the wave-length of the radiation, a quantitative comparison of the wave-lengths of different mono-chromatic radiations can be made.

The problem now resolves itself into an accurate measurement of the angles of reflection at a crystal face. W. H. Bragg (Nature, Jan. 1913, and Proc. Roy. Soc. 1913, 88) constructed an X-ray spectrometer for this purpose. This instrument is similar to the ordinary spectrometer, but instead of the lines of a grating, we have parallel planes of atoms within the crystal, and in place of the telescope, an ionisation

chamber. A fine slit in front of the X-ray bulb allows a beam of rays to fall on the face of the crystal, the reflected beam being detected by the effect produced by it in the ionisation chamber. Both crystal and chamber can turn about the axis of the instrument and can be set independently at any desired angles.

The wave-length of a given X-radiation can immediately be determined by means of the spectrometer in terms of the dimensions of the lattice of the crystal employed for the reflection; but in order to obtain the absolute value of the wave-length, it is necessary to know the structure of the crystal. A knowledge of the structure leads to the absolute value of the spacings of planes parallel to any one face of the crystal, and by the aid of the relation $n\lambda=2d \sin \theta$ the absolute wave-length of the radiation can be calculated.

§ (2) **Crystal Structure.** With a view to arriving at the absolute wave-length of X-rays, W. L. Bragg (Proc. Roy. Soc. 1913, 89) undertook a detailed examination of the halogen salts NaCl, KCl, and KBr. These crystal are isomorphous, and should therefore possess similar arrangement of atoms. Both the photographic and the spectroscopic methods were employed in the investigation. The results obtained with both methods seemed at first to indicate that the crystals belonged to different elementary point systems of cubic symmetry, of which there are three possible, namely, those containing (1) points at each corner of the elementary cube, (2) points at each corner and one at the centre of the cube, and (3) points at the corners and at the centres of the cube faces. The Laue pattern obtained with KCl indicated the simplest arrangement ((1) above), the spots being all nearly of equal intensity, whilst that with KBr pointed to a face centred lattice ((3) above), but NaCl was more complex and did not conform with either of the two foregoing arrangements. These apparently conflicting results are simply explained, if it be assumed that the diffracting centres are single atoms, and that the weight of an atom defines its effectiveness as a diffracting centre, atoms of equal weight being treated as equivalent.

Consider the case of KBr and imagine atoms of Br at each corner of the cube, and at the

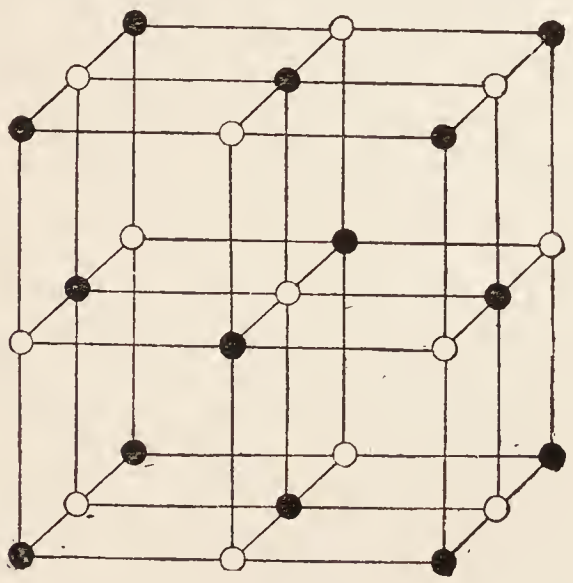


FIG. 12.

centre of each face, and atoms of potassium at the middle of each edge and at the centre of the cube. This arrangement is equivalent to two interpenetrating face centred cubic lattices containing Br and K atoms respectively. The Br atom being much heavier than the K atom, the Br lattice will have a preponderating influence on the pattern obtained. In this case the behaviour of the crystal towards X-rays will approximate that of a face centred lattice. In the KCl crystal, Cl atoms take the places formerly occupied by Br atoms in the lattice, and since Cl and K atoms are of nearly equal weight, the crystal will now behave as if the atoms were arranged in the simplest cubical array, *i.e.* an atom at each corner of the elementary cube. Lastly, in the case of NaCl, since the difference between the weights of Na and Cl is neither as small as that between K and Cl nor as great as that between Br and K, both the Na lattice and the Cl lattice will contribute different but appreciable amounts to the effect produced, and in consequence the resulting pattern will appear more complicated than in either of the two other cases. These deductions fit the facts as revealed by the Laue photographs.

§ (3) **Bragg's Ionisation Method of Crystal Analysis.** The examination of the crystals by the spectrometer method confirmed the above conclusions; in fact, the evidence obtained by this method is more direct and convincing than that obtained by the Laue method. It has been pointed out that the spectrometer gives the spacing between the planes of atoms parallel to the face examined in terms of the wave-length of the radiation employed, so that relative values of the spacings of planes parallel to different faces are readily obtained. Taking the case of KCl, the measuremcnts showed that

$$\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} :: \sin 5{\cdot}22^\circ : \sin 7{\cdot}30^\circ : \sin 9{\cdot}03^\circ$$
$$:: \quad 1 \quad : \quad \sqrt{2} \quad : \quad \sqrt{3}$$

These are the ratios of the spacings in the case of a simple cubic lattice. In the case of NaCl and KBr the measured ratios were as follows :—

$$\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} :: 1 : \sqrt{2} : \sqrt{\tfrac{3}{2}}$$

and these are the ratios of the spacings for a face centred cubic lattice.

By examining the intensities of the different order spectra obtained from each face, we can go a step further and deduce knowledge as to the atoms which the planes contain. The intensities of the spectra from the (100) and (110) faces of both KCl and NaCl fall off at the same rate, namely:

$$I_1 : I_2 : I_3 : I_4 :: 100 : 30 : 7 : 3$$

This may be taken as the normal rate of fall of intensity of the spectra when consecutive reflecting planes are identical and equi-spaced. The spectra from the (111) faces of these crystals decline in intensity at different rates, however; in the case of KCl the rate of decline is the same as for the other faces, whereas in NaCl the spectra fall off at an abnormal rate as follows :—

$$I_1 : I_2 : I_3 : I_4 :: 20 : 100 : 0 : 6$$

These rates of fall of intensity are readily explained if W. H. Bragg's Law is assumed, namely, that planes have equal reflecting power, when their masses per unit area are equal, no matter how the weight is made up or distributed

in the plane. In KCl the (111) planes are alternately made up of K and Cl atoms. Since, however, the weights of K and Cl are approximately the same, consecutive planes are almost identical as to their reflecting power, and in consequence the fall of intensity is normal and the same as that in the case of the (100) and (110) planes, each of which contains equal numbers of K and Cl atoms, and are therefore identical. The (111) planes of NaCl are alternately made up of Na and Cl atoms, and are therefore differently weighted. Calculation shows that this difference in weight is just sufficient to account for the abnormality actually observed in the rate of decline of intensities of the spectra from the (111) planes of this crystal.

Further, the angle at which the first order spectrum from the (111) face of KCl appears is about twice that at which the first spectrum from the (111) face of NaCl is found. This fact follows directly from the above conclusions; in NaCl the spacing between similar planes is about twice that in the case of the (111) planes of KCl, regarding K and Cl planes as similar, and in consequence the first order spectrum makes its appearance in the former case at an angle which is about twice as great as that of the first order spectrum in the latter case. This might be stated otherwise: in KCl the odd order spectra are entirely obliterated whilst in NaCl they are observable, but of small intensity compared with the even order spectra.

The above arrangement of the atoms assumed for the three crystals NaCl, KCl and KBr, is therefore amply justified by the results of the two methods of investigation. Having arrived at the structure of the crystals, it is a simple matter to calculate the dimensions of the lattices.

Consider the case of NaCl. A unit cube of the lattice just found for this crystal has four points associated with it. Each unit cube contains eight smaller cubes whose side is d_{100}. Hence each small cube is associated with half a point, or in other words, each small cube is associated with half a molecule. If ρ is the density, and M the molecular weight of NaCl, and m the mass of the hydrogen atom, then

$$\tfrac{1}{2}\mathrm{M}m=(d_{100})^3\rho$$

$$i.e.\ d_{100}=\sqrt[3]{\frac{\mathrm{M}m}{2\rho}}$$

For NaCl, M=58·50, ρ=2·17, so that

$$d_{100}=2\cdot80\times10^{-8}\text{ cm.}$$

if m is taken as $1\cdot64\times10^{-24}$ gms.

With the aid of this absolute value of the dimension of the lattice, and the knowledge of the angle of reflection of any given wave-length at the (100) face, the absolute value of that wave-length can be determined by means of the relation $n\lambda=2d\sin\theta$.

There is one point to be emphasised regarding the foregoing conclusions. It has been assumed that the points of the lattice contain single atoms in each case. These points may possibly contain molecules or a group of atoms or molecules. If this were the case the absolute dimensions of the lattice would be different from those obtained above.

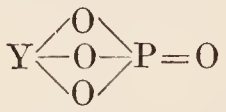
It will be seen from the above brief account that the method of determining crystal structure by the spectrometer may be divided up into two parts: (1) the determination of the values of the angles of reflection from different faces of the crystal, and (2) the determination of the relative intensities of the different order spectra. This latter determination supplies an explanation of the effects produced both by want of similarity between planes which are uniformly spaced (*e.g.* the (111) planes of NaCl), and by a peculiar arrangement of planes which are otherwise similar (*e.g.* the (111) planes of the diamond in which every plane is three times as far from its neighbour on one side as from its neighbour on the other). This method therefore leads to the allocation of definite positions to the atoms in the lattice, and in this respect scores greatly over the Laue photographic method which can only supply information concerning the nature of the lattice, and that to a very limited degree.

For a full account of the irregularities observed in the intensities of the spectra from different crystals and the ingenuity displayed to arrange the atoms within the crystals so as to fit in satisfactorily with these irregularities, the reader is referred to W. H. and W. L. Bragg's book on "X-rays and Crystal Structure," and to the following original papers by the same authors: W. H. and W. L. Bragg, Proc. Roy. Soc. 1913, 89, 277; W. L. Bragg, Proc. Roy. Soc. 1913, 89, 468; W. H. Bragg, Proc. Roy. Soc. 1913, 89, 575; W. H. Bragg, Phil. Mag. Aug. 1915; W. H. Bragg, Roy. Soc. Phil. Trans. July, 1915.

W. L. Bragg (Phil. Mag. Sept. 1914) has solved the structure of copper. The faces of the natural crystal used were prepared by etching them deeply with nitric acid, after which treatment the crystal could be examined with the X-ray spectrometer. The investigation showed that the atoms in copper are arranged in a face-centred cubic lattice. Later, L. Vegard (Phil. Mag. July, 1916) showed that crystals of silver, gold, and lead have identically the same structure as copper.

From an examination of the structure of the minerals zircon, rutile, and cassiterite, L. Vegard (Phil. Mag. Nov. 1916) found that these substances may be represented by the constitution formulæ $ZrO_2{\cdot}SiO_2$, $(TiO_2)_2$. and $(SnO_2)_2$ respectively. The atoms of xenotime (YPO_4) were also found to be arranged in a lattice of the zircon type, and the substance should by analogy have the constitution formula $YO_2.PO_2$.

If xenotime be regarded as a phosphate its chemical constitution formula would be



which puts one of the oxygen atoms in a singular position, and if the valency units are to indicate forces the Y atoms would be attracted to the P atoms so far as chemical attraction is concerned only by means of the oxygen atoms. This chemical constitution formula gives no indication as to the true arrangement of the atoms. Hence, although it is found that the constitution of the solid state of zircon, rutile, and cassiterite should be $ZrO_2{\cdot}SiO_2$, $(TiO_2)_2$, and $(SnO_2)_2$ respectively, it cannot be concluded that these are adequate expressions for the chemical properties of the substances.

The crystalline structure of the isomorphous alkali sulphates K_2SO_4, $(NH_4)_2SO_4$, Rb_2SO_4, and Cs_2SO_4 has been investigated by Ogg, and Hopwood (Phil. Mag. Nov. 1916). Their results show that the elementary cell of each crystal in the series contains four molecules, and that the space lattices of the crystals are strictly comparable with one another. The volume of the unit rhomb of each of the crystals is given in the following table :—

Crystal.	Volume of unit rhomb.
K_2SO_4	$425{\cdot}78 \times 10^{-24}$ c.c.
$(NH_2)_2SO_4$	485·71 cc.
Rb_2SO_4	481·14 ,,
Cs_2SO_4	554·88 ,,

The substitution of two atoms of cæsium for two atoms of potassium causes double the distension of structure that the substitution of ten atoms of the radical groups $2NH_4$ does. Also two atoms of rubidium replace ten atoms of the radicle groups $2NH_4$ without any opening up of the structure. On the Valency Volume Theory of Pope and Barlow each valency in a given compound is supposed to have the same volume, and therefore the atomic volumes of combined elements should be directly proportional to their valencies. In the case of the two salts Rb_2SO_4 and $(NH_4)_2SO_4$, the sum of the valencies is 12 and 24 respectively, if the valency of N is taken as 2, so that the volume of the unit rhomb of $(NH_4)_2SO_4$ should be twice that of a unit rhomb of Rb_2SO_4 on this theory. The fact that X-ray spectrometer measurements show them to be equal indicates that the valency volume theory is not universal in its application.

A. E. H. Tutton (Proc. Roy. Soc. Feb. 1917), from observation of topic axial ratios and molecular volumes, had already concluded that the structure of Rb_2SO_4 was similar to that of $(NH_4)_2SO_4$, and that the lattices were practically identical. This conclusion is confirmed by X-ray measurements.

§ (4) **Powder Method of Crystal Analysis.** The methods of crystal analysis so far described are applicable only to individual crystals of appreciable size, sufficiently free from twinning and distortion and sufficiently developed to allow the determination of the direction of their axes. Such large crystals are somewhat difficult to obtain, and to grow them takes time. Debye and Scherrer (Phys. Zeits. 17, 277, 1916), and Hull (Phys. Rev. 10, 661, 1917) independently developed a method which does not require large crystals for the solution of their atomic structure by X-ray analysis. The quantity of material required in this method is only about 0·005 c.c. and is employed in powder form. Extreme purity is not essential, and a large admixture of uncombined foreign material, 20 p.c. or even 50 p.c., is allowable, provided it is amorphous or of known crystalline structure. In this method a small quantity of the finely powdered material is placed in a tiny glass tube situated in the path of a beam of X-rays which has been rendered monochromatic by passing it through a suitable filter. The rays reflected at the different faces of the small crystals in the tube appear on a photographic film upon which they fall as a series of irregularly spaced lines, the positions of which suffice to solve the structure of the material.

§ (5) **Crystal Structure of the Elements.** The powder method has proved exceedingly useful in examining the crystal structure of the elements, the structures of a large number of which have been solved. Table I. is due to Hull (J. Franklin Inst. Feb. 1922), and contains the structures as well as the atomic radii of those elements that have so far been investigated. The atomic weights and atomic numbers are also included for reference. Some of the elements crystallise on two systems—this is indicated in the table (see pages 628, 629).

It will be observed that elements in the same vertical column of the table all have the same crystal structure. The only exceptions are iron in group 8, and thorium and lead in group 4.

Glucinum is found to possess a hexagonal close-packed structure, and therefore belongs rather with Mg, Zn, and Cd, than with Ca, Sr, and Ba, the first three being hexagonal, all with axial ratio greater than 1·58, and increasing with the atomic number, whereas Ca, the only member of the second three which has been analysed, has cubic symmetry.

The face-centred cubic elements are found mainly in the right-hand columns of groups 1 and 8, that is, in the middle of the long periods. The elements immediately preceding and following these middle elements, viz. the left column of group 8 and the right column of group 2, are hexagonal close packed. Still lower in the long periods, in groups 5 and 6 (left), the elements are all centred cubic. Finally the elements of group 4 are all tetrahedral in the right column and hexagonal closed packed in the left.

The table clearly shows that crystal structure is the same periodic function of atomic number as is chemical behaviour.

The atomic radii given in the table have been calculated from the observed crystalline structure of the material, assuming that the atoms are spheres of definite diameters, packed together as closely as possible.

§ (6) **Crystal Structure of Compounds.** Table II. (page 630), contains a list of the crystal structure of compounds that have been analysed by X-rays.

§ (7) **Application of Powder Method to Chemical Analysis.** In addition to the solving of crystalline structure, the powder method of X-ray analysis has been employed for chemical analysis. Use is made of the fact that substances with different crystalline structure will give entirely different patterns of spectral lines. It is also possible to distinguish between two substances of similar crystal structure, since no two substances have exactly the same molecular volume. Thus lithium, sodium, and potassium fluorides, sodium and potassium chlorides and magnesium oxide have all the same arrangement of atoms in their crystals and all give precisely similar patterns of lines, but the magnification or spread of the pattern is different for each one, being inversely proportional to the cube root of the molecular volume, and consequently these substances are easily distinguishable. A further distinguishing feature is the relative intensity of the different lines which differs greatly even in the most closely related

TABLE I.—MENDELEJEFF'S PERIODIC SYSTEM OF THE ELEMENTS.

Group 0 — —	Group 1 E_2O —	Group 2 EO —	Group 3 E_2O_3 —	Group 4 EO_3 EH_4	Group 5 E_2O_5 EH_3	Group 6 EO_3 EH_2	Group 7 E_2O_7 EH	Group 8 EO_4 —		
	H (1) 1·008	H.C.P. C=1·58 R= 2·23 / 2·21		Rhomb. C=2·75 R=0·75						
He (2) 4·00	C.C. **Li** (3) 6·94 R=1·51	**Be** (4) * 9·1	**B** (5) 10·9	**C** (6) 12·008	**N** (7) 14·08	**O** (8) 16·00	**F** (9) 19·0			
				Dia. R=0·77						
Ne (10) 20·2	**Na** (11) 23·00 C.C. R=1·86	H.C.P. C=1·633 R=1·61 **Mg** (12) 24·32	F.C.C. R=1·43 **Al** (13) 27·1	Dia. R=1·17 **Si** (14) 28·3	**P** (15) 31·04	**S** (16) 32·06	**Cl** (17) 35·46	C.C. R=1·234	{H.C.P. F.C.C.} R=1·257	F.C.C. R=1·252
Ar (18) 39·3	**K** (19) 39·10 C.C. R=2·25	**Ca** (20) 40·07 F.C.C. R=1·96	**Sc** (21) 45·1	**Ti** (22) 48·1 H.C.P. C=1·59 R= 1·48 / 1·45	**V** (23) 51·0	**Cr** (24) 52·0 C.C. R=1·254	**Mn** (25) 54 93	**Fe** (26) 55·84	**Co** (27) 58·97	**Ni** (28) 58·68
	F.C.C. R=1·27 **Cu** (29) 63·57	H.C.P. C=1·86 R= 1·335 / 1·460 **Zn** (30) 65·37	**Ga** (31) 70·1	**Ge** (32) 72·5	**As** (33) 74·96	**Se** (34) 79·2	**Br** (35) 79·92	H.C.P. C=1·59 R= 1·342 / 1·320	F.C.C. R=1·350	F.C.C. R=1·397
Kr (36) 82·92	**Rb** (37) 85·45	**Sr** (38) 87·63	**Yt** (39) 89·33	**Zr** (40) 90·6 H.C.P. C=1·59 R= 1·59 / 1·62	**Cb** (41) † 93·1	**Mo** (42) 96·0 C.C. R=1·360	(43)	**Ru** (44) 101·7	**Rh** (45) 102·9	**Pd** (46) 106·7
	F.C.C. R=1·43 **Ag** (47) 107·88	H.C.P. C=1·89 R= 1·480 / 1·646 **Cd** (48) 112·40	F.C.Tetr. C=1·06 R= 1·62 / 1·66 **In** (49) 114·8	Grey Dia. R=1·597 **Sn** (50) 118·7	**Sb** (51) 120·2	**Te** (52) 127·5	**I** (53) 126·92			
Xe (54) 130·2	**Cs** (55) 132·81	**Ba** (56) 137·37	**La** (57) 139·0	**Ce** (58) 140·25 H.C.P. F.C.C. R=1·82	Rhomb. C=1·324 R=1·51					
		Pr (59) 140·9	**Nd** (60) 144·3	(61)	**Sa** (62) 150·4	**Eu** (63) 152·0				
		Gd (64) 157·3	**Tb** (65) 159·2	**Ho** (66) 163·5	**Ds** (67) 162·5	**Er** (68) 167·7	C.C. R=1·416	C.C. R=1·363		
		Tm (69) 168·5		‡ **Yb** (70) 173 5	**Lu** (71) 175·0	(72)	**Ta** (73) 181·5	**W** (74) 184·0	(75)	
								H.C.P. C=1·59 R= 1·36 / 1·33	F.C.C. R=1·945	F.C.C. R=1·390
								Os (76) 190·9	**Ir** (77) 193·1	**Pt** (78) 195·2

| | | |

Table II.

Crystal Structure of Compounds.

Compound	Type of lattice	Lattice constant (side of elementary cube, hexagon, or rhombohedron)	Closest approach of atoms		Authority
			Name of atom or ion	Distance in Angstrom	
LiF	Simple cubic	4·14	Li–F	2·07	Debye and Scherrer [1]
NH_4Cl at 20°C.	Body-centred cubic	3·859	NH_4–Cl	3·342	Bragg,[2] Barlett and Langmuir [3]
NH_4Cl at 250°C.	Simple cubic	6·533	NH_4–Cl	3·266	,, ,,
NH_4Br at 20°C.	Body-centred cubic	3·988	NH_4–Br	3·453	,, ,,
NH_4Br at 250°C.	Simple cubic	6·90	NH_4–Br	3·45	,, ,,
NH_4I at 20°C.	Simple cubic	7·20	NH_4–I	3·60	Vegard,[4] Bartlett and Langmuir [3]
$NaNO_3$	Rhombohedral	6·06	—	—	Bragg,[5] Wyckoff [6]
NaF	Simple cubic	4·62	Na–F	2·31	Hull [7]
NaCl	Simple cubic	5·628	Na–Cl	2·814	Bragg [5]
NaBr	Simple cubic	5·98	Na–Br	2·99	Davey [9]
NaI	Simple cubic	6·44	Na–I	3·22	,,
$MgAl_2O_4$	Diamond cubic	—	—	—	W. H. Bragg,[10] Nishikawa [11]
MgO	Simple cubic	4·22	Mg–O	2·11	Hull [7]
SiC	Diamond cubic (nearly)	4·356	Si–C	1.88	Burdick and Owen [12]
KF	Simple cubic	5·38	K–F	2·66	Hull [7]
KCl	Simple cubic	6·30	K–Cl	3·15	Bragg [8]
KBr	Simple cubic	6·60	K–Br	3·30	,,
KI	Simple cubic	7·02	K–I	3·51	Davey [9]
$CaCO_3$ (calcite)	Rhombohedral	6·16	Ca–C	3·04	Bragg,[5]
			Ca–O	2·30	Wyckoff [13]
			C–O	1·21	
CaO	Simple cubic	4·84	Ca–O	2·42	Davey [14]
CaF_2	Tetrahedral cubic	5·60	Ca–F	2·38	Bragg [5]
CaS	Simple cubic	5·64	Ca–S	2·82	Davey [15]
TiO_2 (anatase)	Diamond tetragonal	5·27	Ti–O	1·95	Vegard [16]
$MnCO_3$	Rhombohedral	5·62	Mn–C	2·83	Wyckoff [13]
			Mn–O	1·96	
			C–O	1·22	
$FeCO_3$	Same structure and distance as $MnCO_3$.	—	—	—	Wyckoff [13]
Fe_3O_4	Diamond cubic	8·36	—	—	Bragg,[10] Nishikawa
FeS_2	Diamond cubic	5·38	Fe–S	2·25	Bragg [5]
NiO	Simple cubic	4·15	Ni–O	2·07	Davey [15]
Cu_2O	Tetrahedral cubic	4·26	Cu–O	1·84	Bragg,[8] Davey [15]
CuCl	Diamond cubic	5·36	Cu–Cl	2·32	Wyckoff [17]
CuBr	Diamond cubic	5·74	Cu–Br	2·49	,,
CuI	Diamond cubic	6·07	Cu–I	2·63	,,
$CuFeS_2$	Diamond cubic (nearly)	5·23	—	—	Burdick and Ellis [20]
ZnO	Tetrahedral hexagonal	3·22	Zn–O	1·97	Bragg [18]
ZnS	Diamond cubic	5·41	Zn–S	2·25	Bragg [5]
RbBr	Simple cubic	6·92	RbBr	3·46	Davey [9]
RbI	Simple cubic	7·32	RbI	3·66	,,
SrF_2	Tetrahedral cubic	5·77	Sr–F	2·50	Davey [15]
Ag_2O	Tetrahedral cubic	4·70	Ag–O	2·03	,,
AgCl	Simple cubic	5·56	Ag–Cl	2·78	Wilsey [19]
AgBr	Simple cubic	5·78	Ag–Br	2·89	,,
AgI	Diamond cubic	6·53	Ag–I	2·83	,,
CdO	Simple cubic	4·61	Cd–O	2·30	Davey [14]
CdS	Tetrahedral hexagonal	4·16	Cd–S	2·54	Davey [15]

TABLE II.—*continued.*

CRYSTAL STRUCTURE OF COMPOUNDS.

Compound	Type of lattice	Lattice constant (side of elementary cube, hexagon, or rhombohedron)	Closest approach of atoms		Authority
			Name of atom or ion	Distance in Angstrom	
SnS	Tetrahedral hexagonal	3·60	Sn–S	2·20	Davey [15]
CsCl	Body-centred cubic	4·10	Cs–Cl	3·55	Davey and Wick [22]
CsBr	Body-centred cubic	4·33	Cs–Br	3·75	,, ,,
CsI	Body-centred cubic	4·57	Cs–I	3·96	Davey [9]
$CsClI_2$	Rhombohedral	—	—	—	Wyckoff [21]
BaF_2	Tetrahedral cubic	6·20	Ba–F	2·69	Davey [15]
BaS	Simple cubic	6·40	Ba–S	3·20	,,
TlCl	Body-centred cubic	3·85	Tl–Cl	3·34	Davey and Wick [22]
PbS	Simple cubic	5·80	Pb–S	2·90	Davey [15]

[1] Debye and Scherrer, Physik. Zeitschr. 19, 474, 1918.
[2] W. H. and W. L. Bragg, X-rays and Crystal Structure, 158.
[3] Bartlett and Langmuir, J. Amer. Chem. Soc. 43, 85, 1921.
[4] Vegard, Phil. Mag. 33, 395, 1917.
[5] W. L. Bragg, Proc. Roy. Soc. A. 89, 468, 1914.
[6] Wyckoff, Phys. Rev 16, 149, 1920.
[7] Hull, Proc. A.I.E.E. 38, 227, 1919.
[8] W. H. and W. L. Bragg, X-rays and Crystal Structure, 91.
[9] W. P. Davey, Phys. Rev. 18, 102, 1921.
[10] W. H. Bragg, Phil. Mag. 30, 305, 1915.
[11] S. Nishikawa, Tokio Sug. But. Kizi, 8, 199, 1915.
[12] C. L. Burdick and E. A. Owen, J. Amer. Chem. Soc. 40, 1749, 1918.
[13] R. W. G. Wyckoff, Amer. J. Sci. 50, 317, 1920.
[14] W. P. Davey, Phys. Rev. 15, 333, May, 1920.
[15] W. P. Davey, Amer. Phys. Soc. Nov. 1921.
[16] L. Vegard, Phil. Mag. 32, 505, 1916.
[17] R. W. G. Wyckoff, J. Amer. Chem. Soc.
[18] W. L. Bragg, Phil. Mag. 39, 647, 1920.
[19] R. B. Wilsey, Phil. Mag. 42, 262, 1921.
[20] Burdick and Ellis, J. Amer. Chem. Soc. 39, 2518, 1917.
[21] Wyckoff, J. Amer. Chem. Soc. 42, 1100, 1920.
[22] Davey and Wick, Phys. Rev. 17, 403, 1921.

compounds depending upon the relative shapes and sizes of the atoms in the compound.

If a mixture of substances is exposed to the radiation, each component produces its pattern independently of the others, so that the photograph obtained with a mixture is the superposed sum of the photographs that would be obtained by exposing each of the components separately for the same length of time. This law applies quantitatively to the intensities of the lines as well as to their positions, so that the method is capable of development for quantitative analysis. By means of long exposures, very small impurities can also be detected. A full account of this work may be found in "X-ray Studies," 1919, published by General Electric Company, Schenectady.

§ (8) **Crystal Structure of Alloys.** Owen and Preston (Proc. Phys. Soc. 35, 101, Feb. 1923) have investigated the structure of metal crystals, employing a modification of the powder method of analysis. Instead of reducing the metal, the crystalline structure of which is required, to a fine powder, a plate of the metal is taken and examined by means of the ionisation X-ray spectrometer in a manner similar to that adopted by Bragg. This method has been applied also with success to the examination of intermetallic compounds and alloys (Proc. Phys. Soc. Oct. 1923).

The structure of alloys has also been investigated among others by Bain (Chem. and Met. Eng. Jan. 10, 65, 1923), Westgren and Phragmen (J. Inst. Iron and Steel, 105, 241, 1922), and McKeehan (Phys. Rev. 20, 424, Nov. 1922), all of whom employed the photographic method.

§ (9) **Structure of Organic Crystals.** Another branch which has been opened out by X-ray analysis is the study of the structure of organic crystals. Several of the organic compounds have been examined by W. H. Bragg and his colleagues, and a good deal of information has been obtained regarding the system which governs the packing. Amongst the crystals whose atomic structures have been solved are naphthalene, anthracene, and tartaric acid. A striking physical property of tartaric acid is its power of rotating the plane of polarisation of light. It has been surmised that this was due to a spiral arrangement in the structure. This has been confirmed by X-ray analysis which shows the presence of two spirals. One is in the interior of the molecule, and is therefore not destroyed when the crystal is dissolved, which accounts for the fact that tartaric acid in solution can exercise its rotatory power. The second spiral is a twist brought about by the necessity of fitting the molecules into their places. It is a peculiarity of the crystal structure, not of the molecule. It is a right-handed screw if the first is a left-handed screw, and *vice versâ*. Also it appears to be more powerful in its effect on the light, so that when the tartaric acid as a crystal rotates light in one sense, in solution it rotates light in the opposite sense.

§ (10) **X-ray Spectra.** When a beam of rays from an ordinary X-ray bulb is analysed by the

X-ray spectrometer, it is found to consist of a continuous spectrum of radiation upon which are superposed a few wave-lengths which stand out prominently from the rest, these being the characteristic wave-lengths of the metal of the anticathode. In the case of a bulb with platinum anticathode, W. H. Bragg (Proc. Roy. Soc. 1913, 89, 246) calculated that the strongest line in the spectrum had a wave-length of $1{\cdot}10 \times 10^{-8}$ cm., assuming the atomic distances of rock salt experimentally determined by W. L. Bragg. The mass absorption coefficient of this radiation in aluminium was 23·7. This value of the absorption coefficient, according to Barkla's results, corresponds either to a K characteristic radiation from an element of atomic weight 72·5, or to an L characteristic radiation from one of atomic weight 198. The atomic weight of platinum is 195, so that the wave-length measured must be that of the principal line in the L series spectrum of platinum. Bragg found that the K series spectra of Pd, Rh, Cu, and Ni consisted of two prominent lines, and there was a strong similarity observed between the relative spacings of the lines in each spectrum.

§ (11) **Moseley's Law.** Moseley (Phil. Mag. Dec. 1913, and April, 1914) undertook an extensive investigation of the X-ray spectra of about 40 elements, whose atomic weights lie between those of Al (27·1) and Au (197·2). Divergent beams of rays from different anticathodes fell in turn on the face of a crystal of potassium ferrocyanide. The spectra were examined photographically. Those of elements between Al and Ag consisted of two and only two sharply defined lines, which were referred to as the α and β lines. These are spectra of radiations of the K series. Elements ranging from zirconium to gold gave spectra consisting mostly of five well-defined lines, which were referred to as the α, β, γ, δ, and ϵ lines. These are spectra of radiations of the L series. The wave-lengths of the radiations in any one of the sub-series α, β, etc., diminished as the atomic weight increased; but no definite relation was found to exist between these two variables.

It had been suggested by Van den Broek (Phys. Zeits. 1913, 82) that the number representing the order of the elements in the periodic table might be a more fundamental index of quality than the atomic weight. When this quantity (N), called the atomic number, was plotted against the frequencies of the radiations (ν), in any sub-series, Moseley found the following relation:

$$\nu = a(N - b)^2$$

where a and b are constants characteristic of each of the sub-series. This relation was so accurately obeyed that it was possible to predict with confidence the principal lines in the spectrum of any element from Al to Au. Furthermore, known elements were found to correspond with all the natural numbers between 13 and 79, with the exception of four, so that there are four possible elements still undiscovered within the range of elements from Al to Au. These undiscovered elements are situated as follows: (1) between Mo and Ru (N=43), (2) between Nd and Sa (N=61), (3) between Lu and Ta (N=72), and (4) between W and Os (N=75). The gap between Lu and Ta has already been filled by the recent discovery of the new element Hafnium (N=72).

The atomic number N has been identified with the number of positive units of electricity contained in the atomic nucleus. In Rutherford's atom, the positive nucleus is surrounded by electrons carrying an equal negative charge to the nucleus, and rotating about it. Since each electron carries one unit of negative electricity, the atomic number may also be defined as the number of electrons in the atom. Thus for hydrogen, N=1, for helium N=2, etc.

The arrangement of the elements in order of atomic numbers does not follow the order of atomic weights throughout the entire list. There are departures when the latter does not agree with the sequence of chemical properties as required by the periodic law. Thus, nickel has an atomic weight of 58·7, whereas certain chemical properties and its behaviour in experiments on radioactivity indicate that it should lie between cobalt (59·0) and copper (63·6). The atomic numbers of the three elements Co, Ni, and Cu have been taken as 27, 28 and 29 respectively, and it is found that the wave-lengths found for them agree accurately with this order. Similarly, argon is placed before potassium and tellurium before iodine.

§ (12) **K, L, and M Series Spectra of the Elements.** A careful examination of the second and third order spectra of Rb, Pd, and Ag from a face of the diamond, carried out by W. H. Bragg (Phil. Mag. March, 1915) with the spectrometer, revealed the fact that each of the lines previously observed in the K series radiations of these elements was composed of two definite wave-lengths, so that the K series spectra consist of four lines, these were referred to as α_1, α_2, β_1, and β_2 lines. Lebard-Ledoux and Dauvillier (Compt. rend. 1916, 163), employing a different method, also observed four lines in the K series radiation of tungsten. Later Siegbahn (Phil. Mag. June, 1919), Hjalmar (Zeit. f. Physik, 1 B. 5 H. 1920), Dolejsek (C. R. Feb. 1922), Stensson and Stenstrom (Bulletin of the National Research Council, Nov. 1920), have found as many as eight lines in the K series spectra of the lighter elements.

The spectra of a number of elements were examined photographically in detail by De Broglie (Compt. rend. 1913, 157). In his method a slowly rotating crystal is used to reflect the rays. By this means a full spectrum of the radiations contained in the incident beam is recorded on a photographic plate. Rock salt was used as the reflector. The photographs obtained showed two distinct phenomena: (1) The action of the rays on the photographic plate itself. (2) The effect of interposing a given element in the path of the rays. The emulsion of the film contains among others the two heavy elements silver and bromine. There are radiations in the incident beam capable of stimulating the characteristic radiation of these elements, and when this occurs there is a marked increase in the number of corpuscles emitted. These liberated corpuscles help to accelerate the chemical action which ordinarily takes place in the photographic film, with the result that there is an increased blackening of the film at those regions of the spectrum corresponding to the K radiations of Br and

Ag. This effect shows itself in the form of dark bands, which are sharply defined and intense on the long wave-length side and shade off for short wave-lengths. The sharply defined edges give the wave-lengths of the radiations, which are able to excite the characteristic radiations of the two elements mentioned. As to the second effect a thin sheet of metal placed in the beam selectively absorbs those radiations which stimulate its characteristic radiations. These radiations are therefore removed from the beam, with the result that there is now a light band in the spectrum, sharply defined on the long wave-length side, which enables a measurement to be made of the wave-length of the radiation necessary to excite the K radiation of the element. The conclusion arrived at from these observations was that all the elements possess in general a band of absorption for wave-lengths just shorter than those of their own characteristic radiations, a result which had previously been stated by Barkla and Sadler. The investigation was extended to compounds. When the spectra of iodine, potassium iodide, and lead iodide were examined it was found that the iodine band was obtained in the same position in each case. The emission of characteristic radiation by an atom of iodine is therefore independent of its state of combination, *i.e.* it is purely an atomic phenomenon.

The photographs taken of the L radiation showed that this is more complex than the K radiation.

Siegbahn and Friman (Phys. Zeits. 1916, 17, and 61), examining the L series spectra of the heavy elements from tantalum to bismuth, and the rare earths, found that they all consisted of a group of at least eleven lines, which could be traced from one to the other. The frequencies of the radiations agreed with those deduced by Moseley's law to within 1 p.c. They found the atomic numbers of radium and polonium (electrolytically deposited on copper) to be 88 and 84 respectively. Only two lines in the spectrum of polonium and one in that of radium could be measured with accuracy.

Siegbahn and Friman (Phys. Zeits. 1916, 17, 176), using a spectrograph *in vacuô*, detected a very soft radiation, which they called the M series radiation, emitted by the heavier elements. Further measurements of the wave-lengths of the lines in the M series have been carried out by Stenstrom (Thesis, Lund, 1919), and Karcher (Phys. Rev. April, 1920).

§ (13) **Diffraction of Gamma Rays.** Rutherford and Richardson (Phil. Mag. May, 1913) have shown that RaC emits one and RaB three types of γ-radiation, each of which is exponentially absorbed in Al. These radiations have been examined by Rutherford and Andrade (Phil. Mag., May and August, 1914) by reflection at a face of rock salt. The source of γ-radiation was a thin-walled α-ray tube, containing about 100 millicuries of emanation in equilibrium with its products A, B, and C.

A diverging cone of rays fell on the crystal and the distribution of the reflected radiation was examined by the impression produced on a photographic plate placed 10 cm. from the centre of the crystal.

The soft rays emitted by RaB were first investigated. Difficulties were encountered on account of (1) the long exposure necessary to obtain an impression on the plate; (2) the direct action of the penetrating γ-rays from RaC which had to be screened off by thick pieces of lead; and (3) the effect of the primary and secondary β-rays. The effects of the latter were reduced by placing the source and crystal in a magnetic field of about 2,500 gauss.

The spectrum of the γ-radiation from RaB was found to consist of twenty-one lines having wave-lengths ranging from $0{\cdot}793\times10^{-8}$ cm. to $1{\cdot}365\times10^{-8}$ cm., the two strongest lines being reflected from the (100) face of rock salt at the angles 12·05° and 10·05°, and therefore having wave-lengths $1{\cdot}175\times10^{-8}$ cm. and $0{\cdot}982\times10^{-8}$ cm. respectively.

RaB is identical in chemical properties with Pb, and on the nucleus theory of the atom this is explained by assuming that the nuclear charges are the same for both. If the charge on the nucleus decides the characteristics of the high frequency spectra of an atom, as we are led to believe from the results of Moseley on the X-ray spectra of the elements, then the γ-radiation spectrum of RaB should be similar to that of lead. It may be deduced from Moseley's results that lead should have a nuclear charge of $82e$, and that the main line in its X-ray spectrum should be reflected by the (100) face of rock salt at a glancing angle of 12·07°. This is in close agreement with the value 12·05° quoted above for the angle of reflection of the strongest line observed in the RaB spectrum.

In further experiments the γ-ray spectra of RaB and lead were compared under as nearly as possible identical conditions. The spectrum in the latter case was obtained by exciting γ-rays in a thin strip of lead by allowing a strong pencil of β-rays to fall upon it. Owing to experimental difficulties only two lines of lead could be measured. These were reflected at glancing angles of 10·03° and 12·00° from the (100) face of rock salt, which agree very closely with the values found for the glancing angles of the two strong lines in the RaB spectrum.

The wave-lengths found by Rutherford and Andrade for the two strong lines of RaB agree within 1 in 300 with the lines in the Z spectrum of the L radiation of lead, measured by Sigbahn, which is further confirmation of the fact that these two substances are isotopic.

The wave-lengths of the penetrating γ-radiation from RaC are much shorter than any previously measured. They were found to range from $0{\cdot}71\times10^{-9}$ cm. to $1{\cdot}96\times10^{-9}$ cm. Comparing these with the wave-lengths in the spectra of the radiations of the elements measured by Moseley, it is concluded that RaC emits another type of characteristic radiation which is of higher frequency than that of the K radiation. Barkla has also discovered a radiation of very high frequency emitted by the light elements which he called the J series radiation. It is possible that the penetrating γ-radiation emitted by RaC belongs to this series.

§ (14) **Heat Motion of the Atoms.** In the foregoing the atoms in the crystal have been supposed to be at rest, but they are actually in motion, and Debye (Verh. d. D. Phys. Ges. 1913, xv. 678, 738, 857; Ann. d. Phys. 1914, 49) has pointed out that this heat motion has an essential influence on the interference phenomena

observed. He calculated this effect and arrived at the conclusion that the interference intensity decreases exponentially with (*a*) increasing angle of reflection; (*b*) increasing temperature; (*c*) decreasing wave-length; and (*d*) decreasing characteristic temperature. This characteristic temperature is used to denote the temperature at which the substance of the crystal stands in relation to its specific heat. Thus for KCl, CaF_2, and diamond, the characteristic temperatures are 219° A, 474° A, and 1830° A respectively. A high value of the characteristic temperature implies a small thermal movement and a small capacity for heat.

The diagram shows the 2nd and 3rd order spectra of a rhodium line reflected at the (100)

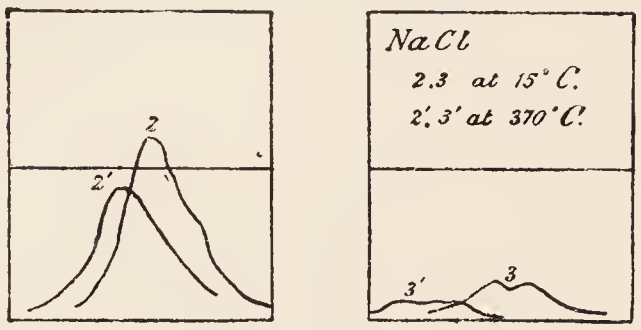


FIG. 13.

face of rock salt at temperatures of 15°C. and 370°C. (W. H. Bragg, Phil. Mag. 1914). From the displacement of the spectra towards the left the increase in the spacings due to the increase in temperature can be calculated. It will also be observed that the intensities of both the 2nd and the 3rd order spectra are diminished by the rise in temperature, and the 3rd more than the 2nd. This is in strict agreement with Debye's theory. On the whole, however, the experimental results seem to show a rather larger change of intensity than that accounted for by Debye's formula.

The results of Backhurst (Roy. Soc. Proc. 102, Dec. 1922), who extended the investigation to higher temperatures, showed general agreement only with theory. In the case of aluminium a very marked decrease of intensity was observed with rise of temperature and fair agreement with theory obtained for (100) and (222) spectra. For carborundum the decrease of intensity with rise of temperature was much greater for the higher order spectra, and diamond showed no measurable decrease of intensity.

The fact that the increase in the spacings between the planes in a crystal when its temperature is raised can be measured accurately with the X-ray spectrometer, makes it possible to measure the coefficient of expansion of the crystal in different directions. This can be done by using a crystal only 2 or 3 sq. mm. in area.

§ (15) **Absorption of X-rays by Matter.** The analysis of a beam of X-rays into its constituent radiations by reflection at a crystal face provides a means of obtaining radiation of definite wave-length, and of such intensity as to enable its absorption coefficient in different materials to be measured with accuracy. X-radiation may lose its energy in passing through matter in two ways: (1) by the production of scattered radiation; and (2) by the production of corpuscular radiations and the characteristic (or fluorescent) X-radiations that accompany them. These two processes take place simultaneously but they appear to be quite independent of one another. This gives rise to two distinct absorption coefficients, which have been termed the scattering coefficient and the fluorescent coefficient. Defining the atomic fluorescent absorption coefficient $\left(\frac{\tau}{\rho}\right)$ as the proportion of the energy of an X-ray pencil which is absorbed in the production of corpuscular radiations (together with the fluorescent X-radiations that accompany them), in crossing a surface on which lies one atom to every sq. cm., it is found that the following relation exists: $\left(\frac{\tau}{\rho}\right)=CN^4\lambda^3$, where N is the atomic number of the absorber and λ the wave-length of the radiation absorbed. C is a constant over certain ranges, but changes in value abruptly at critical points. The relation is independent of the scattering coefficient.

E. A. O.

RADISH, *Raphanus sativus* (Linn.). Several varieties have been distinguished, *e.g. R. s. griseus*, *R. s. radicula*, and *R. s. tristis*. The first produces seeds rich in oil, the second yields very small edible tap roots, whilst the third is valued for its relatively large tap root. The roots of all possess the well-known pungent flavour due to allyl *iso*-thiocyanate. König gives, as the composition of the edible portions of the roots—

	Water	Protein	Fat	Sugar	Other N-free ext.	Crude fibre	Ash
R. s. tristis .	86·9	1·9	0·1	1·5	6·9	1·6	1·1
R. s. radicula	93·0	1·2	0·2	0·9	2·9	0·8	0·7

According to Saiki (Zeitsch. physiol. Chem. 1906, 48, 469), radishes contain a powerful diastatic ferment, which can be obtained in the form of a yellowish-white, somewhat hygroscopic powder. Little or no starch is present in the root under normal conditions, but when the plants are watered with a solution containing from 4 to 10 grms. of sodium chloride per litre, the roots contain considerable quantities of starch (Lesage, Compt. rend. 1891, 113, 373). Boric acid has been found in radishes (Gessend, Ann. Argon. 1891, 17, 352). By distilling an aqueous extract of *Raphanus niger* (Mill.) (*R. sativus*), Moreigne (J. Pharm. Chim. 1896, 4, 10) obtained a crystalline substance, *raphanol* $C_{29}H_{58}O_4$, melting at 62° and soluble in ether, chloroform, benzene, or light petroleum.

According to Kellner (Landw. Versuchs. Stat. 1883, 30, 42), a gigantic variety of radish, single roots of which attain a weight of $2\frac{1}{2}$ to 3 kilos., is much esteemed as a vegetable in Japan. He found this to contain—

Water	Protein	Fat	Soluble carbohydrates	Crude fibre	Ash
93·45	0·67	0·07	4·40	0·77	0·43

about two-thirds of the total nitrogen being present as real proteids. The ash contained—

K_2O	Na_2O	MgO	CaO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
46·4	2·4	4·7	9·4	0·6	10·1	13·1	2·6	11·9

The proportion of sulphur, in organic combination in the roots, varies from 0·22 to 0·07 p.c.

Another Japanese species, *R. caudatus* (Linn.),

is valued for its seed pods, which are about twice the size of those of the common radish, and are eaten as a salad or pickled in vinegar (Rep. New York Expt. Stat. 1884). According to Sacher (Chem. Zeit. 1910, 34, 1192 and 1333), the skins of the red radish, extracted for a few hours with their own weight of 90 p.c. alcohol, yield a solution which serves as a delicate and useful indicator for acids and alkalis, turning intensely red with the former and green with the latter.

The colouring matter of radishes has been studied by Schudel (Diss. Zürich. 1918). From the peelings of yellowish-red radishes, *Raphanin hydrochloride* is obtained as a lustrous vermillion powder. Raphanin is a diglucoside, easily soluble in methyl alcohol, in water and in warm hydrogen chloride-absolute alcohol. The corresponding anthocyanidin, *raphanidin* is identical with pelargonidin. Violet radishes yielded the pigment *rubin*, a dark carmine-red diglucoside, soluble in hydrochloric acid and in methyl alcohol, but sparingly soluble in ethyl alcohol. *Rubidin* is identical with cyanidin (Chem. Soc. Abstr. 1921, i. 485).

H. I.

RADIUM. Symbol Ra. At.wt. 226. A radioactive element discovered by M. and Mme. Curie in the pitchblende from Joachimsthal (P. Curie, S. Curie and G. Bémont, Compt. rend. 1898, 127, 1215).

Occurrence.—All ores containing uranium also contain radium. In the majority of them, the ratio of radium to uranium is equal to the 'equilibrium ratio' $3{\cdot}2\times10^{-7}$, *i.e.* 320 mgm. radium are present per ton of uranium (*v.* McCoy, Ber. 1904, 37, 2641). According to Lind and Roberts (J. Amer. Chem. Soc. 1920, 42, 1170) the ratio is $3{\cdot}40\times10^{-7}$. Becker and Jannasch, found $3{\cdot}399\times10^{-7}$; Rutherford and Boltwood, $3{\cdot}4\times10^{-7}$. In *autunite*, a hydrated calcium uranium phosphate which occurs in France and Portugal, the proportion of radium is only from 20 to 80 p.c. of the above, radioactive equilibrium not having been established. In American carnotites it is $3{\cdot}33\times10^{-7}$. Geologically, old formations contain a slightly larger radium ratio than the more recent formations (Mlle. Gleditsch, Le Radium, 1911, 8, 256). *Cf.* Büchner, Proc. K. Akad. Wetensch. Amsterdam, 1912, 14, 1063; Joly, Phil. Mag. 1912, [vi.] 23, 201; Fletcher, *ibid.* 1912, 279; Poole, *ibid.* 1920, [vi.] 40, 466.

The extremely delicate emanation test for radium reveals the presence of that element in all common rocks and minerals, and in natural springs, both hot and cold. Most of the celebrated spas contain appreciable quantities of radium or its emanation.

Radium preparations are usually obtained from pitchblende, an impure uranosouranic oxide, occurring in Cornwall, in Bohemia (Joachimsthal), Norway, Gibson County (Colorado), and in East Africa, where pitchblende occurs in pegmatites. These pegmatites in East Africa are worked for mica, along with which are found masses of pitchblende, weighing as much as 30 to 35 kilos. and containing up to 89·5 p.c. of U_3O_8. Fergusonite containing 13·6 p.c. of uranous oxide is also found in the same district. Norway has two deposits, one at Evje (north of Christiansund) and another at Stavanger, but they are only weakly radioactive. The uranium minerals of Cornwall and North Devon are found associated with tin ores and metallic sulphides. The distribution is irregular and the radioactivity weak. At Joachimsthal the pitchblende accompanies cobalt, nickel, and the rare metals. These deposits are very rich and all the radium passes to the residues from the manufacture of uranium colours. One kilo. of pitchblende with 60 p.c. of U_3O_8 has an activity equal to 0·33 mgrm. of radium bromide. The mines can produce 16 to 20 tons of ore annually containing on an average 25 p.c. U_3O_8.

Uranium ores are frequently associated with sulphide ores of the rare metals, copper, cobalt, and nickel, particularly when these are found in tin-bearing granite. The production of radium at Joachimsthal is about 1·8 grms. of the most active salt per annum. This, in 1911, was valued at £28,800, from which must be deducted £720 for expenses (Krusch. Z. prakt. Geol. 1911, 19, 83). In 1915 the Austrian Government radium factory produced about 1·75 grms. of radium compounds valued at £40,000.

While all the radium placed upon the market in the last few years has been produced in Europe, a large portion of this output has come from American ores. At least 20 to 25 tons of high-grade pitchblende have been exported. During the last year, carnotite carrying 28·8 tons of U_3O_8, from which 11·43 grms. of radium bromide could be obtained, were produced. All this ore was shipped abroad for the extraction of radium. The value of the radium salts extracted would be about £106,000. The total supply of radium salts from all other sources was 3·65 grms. of radium chloride, basing the production of the Austrian mines for 1912 upon that of 1911, which is known. Pitchblende has been found in small quantities in Connecticut and in the felspar quarries of North Carolina. Practically the total American output has come from the mines in Quartz Hill, Gilpin County, Colorado. Carnotite consists mainly of potassium uranyl vanadate, but contains also small amounts of barium and calcium compounds. It of necessity carries radium, although it has not yet been definitely established that the uranium and radium are in equilibrium as they are in pitchblende. In carnotite the amount of radium is not far from the equilibrium ratio, and in calculations given above an allowance of 10 per cent. has been made to cover this possible deficiency. The more important deposits are scattered over Colorado and Utah. Carnotite always carries vanadium as well as uranium and radium, but is purchased almost wholly on its radium content, comparatively little being allowed for the vanadium present. Ore of 2 p.c. uranium oxide is now worth approximately $75 per ton f.o.b. New York. In the mining of these carnotite ores it is probable that 5 tons of material capable of concentration are wasted for every ton that finds its way to the market. To develop methods for concentrating these ores is one of the problems before the Bureau of Mines (Parsons, Mining and Eng. World (Chicago), May 10, 1913 (T.R.); J. Soc. Chem. Ind. 1913, 32, 606. See also, U.S. Comm. Rept. July, 27 1915; J. Soc.

Chem. Ind. 1915, 34, 870 ; Loomis and Schlundt, J. Ind. Eng. Chem. 1916, 8, 990).

The working of pitchblende (average uranium content, 45 p.c.) at the Austrian State radium factory, Joachimsthal, by the Curie-Debierne method gives at most 80 p.c. of the radium present, and at the French factory of Armet de Lisle, uranium mica, uranium ochre, carnotite, and autunite, in part decomposed directly with hydrochloric acid, yield above 70 p.c. of their radium content. The Ulzer-Sommer method (J. Soc. Chem. Ind. 1910, 1156) gives yields of 97–98 p.c., and has been carried out on the large scale. The separation of radium and barium is usually effected by fractional crystallisation. In 1914 the total world's output of radium (mostly employed in making pharmaceutical preparations and radiation apparatus) was estimated at 7–8 grms. per annum (Sternlicht, Chem. Zeit. 1914, 38, 49 ; J. Soc. Chem. Ind. 1914, 33, 864).

Material containing radium is first treated with concentrated sulphuric acid, for a longer time (some weeks) at normal temperature or a shorter time (several hours) at boiling temperature ; or it is fused with acid sulphates, and the residue, remaining after repeated washing, is boiled, under pressure, with concentrated solutions of caustic alkalis or alkali carbonates, or is melted therewith ; the melt is treated with water, and, after further repeated washing, the residue is boiled with dilute sulphuric acid. Or, the same effect may be obtained by treating first with alkaline agents and then with acid agents. In either case, a residue of only about $\frac{1}{2}$ p.c. remains, in which nearly all the radium is contained as sulphate, and the process can be carried out in a very short time, and with little difficulty. As an example : 100 kilos. of finely ground pitchblende residue are heated with about 400 kilos. of crude concentrated sulphuric acid for several hours, until the acid begins to fume ; when the dark brown colour of the mixture has changed to light brown or grey, the mass is introduced into 10–20 times the quantity of water, boiled, left to stand, and the solution decanted. The residue is washed twice with water, collected on a filter, dried, and the dry mass, weighing 45–50 kilos., is heated with 130–150 kilos. of commercial sodium hydroxide in iron crucibles, until (generally in 1–2 hours) a uniform melt is obtained, and this is boiled several times with water (about 1000 litres each time), after which it is left to stand, decanted, and filtered. The moist residue is boiled with about 5 kilos. of dilute sulphuric acid (20 p.c.), and is then filtered and washed, about 0·5 kilo. of crude sulphates being obtained. Other examples are given. The crude sulphates may be converted quickly and almost completely into chlorides by fusing with alkali carbonates, washing, filtering, and dissolving the residue in pure hydrochloric acid. The crude chloride obtained by evaporating this solution may, for making bathing preparations, be left to stand alone, or with the addition of other known bath admixtures in solid or liquid form, in air-tight vessels, until the highest activity is reached (Ulzer and Sommer, Vienna, Eng. Pat. 19820, Aug. 30, 1909 ; J. Soc. Chem. Ind. 1910, 29, 1156). When sulphuric acid is used as the solvent in the determination of radium in an ore it is necessary to decompose the ore with a small quantity of nitric acid and then boil the mixture with the addition of sulphuric acid in order to reduce the activity to zero ; for the subsequent collection of the emanation the solution is again boiled and a current of air is aspirated through it. Phosphoric acid may be used in place of sulphuric acid ; the required quantity of the ore is heated with 30 c.c. of 85 p.c. phosphoric acid until the mixture boils quietly, and the boiling is continued for 2 minutes to ensure that the temperature reaches 300°C. The tube is then closed with a rubber stopper carrying two tubes and the emanation is collected subsequently in the same way as when sulphuric acid has been used (C. E. Baumgarten and H. H. Barker, J. Ind. Eng. Chem. 1923, 15, 597–599 ; J. Soc. Chem. Ind. 1923, 42, 1204 A.).

According to Moore (Amer. Inst. Min. Eng. Sept. 1918) the average radium content of commercial (American ?) ores is 5–10 mgrms. per ton. The treatment aims at first obtaining a barium radium sulphate concentrate, which may be effected by several methods. The ore may be boiled with alkaline carbonate solution or fused with the solid salt, whereby uranium and vanadium are rendered soluble. The residue is leached with hydrochloric acid and the solution precipitated with sulphuric acid. In the Radcliffe process the ore is fused with salt cake, the fusion product crushed and agitated with water, and the liquor separated from the heavy unattacked material. The turbid solution is left to settle, when it deposits sulphates of barium, lead, and radium. In the U.S. National Radium Institute, the material is boiled with 40 p.c. nitric acid, in which the alkaline earth sulphates are appreciably soluble. The hot acid solution is rapidly filtered under pressure through a plate of 'filtros' or alundum forming the bottom of an eartherware filter set in a steel shell. The filtrate deposits barium and radium sulphates. The sulphate concentrate which should carry 1 mgrm. of radium per kilo. is reduced by ignition with charcoal, and the resulting sulphide dissolved in hydrochloric acid. Further concentration is effected by fractional crystallisation of the mixed chlorides, and later on of the mixed bromides from acid solution, the radium accumulating in the less soluble fractions (J. Soc. Chem. Ind. 1918, 626A.). Purification of radium salts from barium salts is more efficiently carried out by crystallisation of the bromides than by crystallisation of the chlorides (*cf.* Scholl, J. Amer. Soc. Chem. 1920, 42, 889). The total output of the Standard Chemical Co. (Pittsburgh, Pa.) up to 1920 is reported to be 50 grms. of radium element, and the company is said to be able to produce 50 grms. yearly should the demand justify it. Since 1913 three new radium factories have been started in America and several in France, where an average of 18 grms. of radium per annum was produced during the War (J. Röntgen Soc. July, 1920).

For the opening up of earths poor in radium, *see* Ebler and van Rhyn, Zeitsch. angew. Chem. 1921, 34, 477 ; Chem. Soc. Abstr. 1921, 119, ii. 616.

The carnotites found in the Paradox Valley of Colorado are deposited on and impregnate a fine-grained porous sandstone, and the ore as found has usually the appearance of a dirty, mud-coloured sandstone. It contains from 1·5 to 2·5 p.c. uranium oxide, though occasionally pockets containing ores of 10 and even 18 p.c. uranium oxide are found. Of late years the price of radium salts has fallen since the discovery of radioactive material in the Belgian Congo. Mines of the Paradox Valley have therefore, to a large extent, closed down. It is calculated that Katanga (Belgian Congo) can produce 25 grms. per annum for the next ten years. The amount of radium known to be existing in the world in 1923 was 200 grms. For a detailed description of the American methods of production, *see* H. D. d'Aguiar, Chem. and Met. Eng. 1921, Nov. 2 and 9. The following is an abstract from the account :—

The Production of Radium from Carnotite.

The ore as mined is weighed and tested for uranium content by the electroscope. From the warehouse the ore is sent to the grinding mills, where it is reduced by means of Hardinge or other suitable ball mills to pass 60 mesh.

The analysed ore is sent to the dissolving tanks. The tanks are shallow and about 60 sq. ft. in area. The ore is spread in a layer from 4 to 6 ins. deep on the bottom of the tanks and is then damped carefully with water or weak vanadium-uranium liquor from previous extractions. So prepared, the ore is ready for the extraction of the uranium, vanadium, and radium. This is accomplished by treating the ore with hydrochloric acid. During the addition of the hydrochloric acid the ore is continually turned and agitated so that the acid may act evenly on the entire mass. Sulphuric acid is then added in sufficient quantity to precipitate all barium and calcium. Water or more weak vanadium liquor from previous extractions is then added. The stirring is continued throughout the entire operation. The liquor, which now contains the uranium and vanadium in solution and the barium-radium sulphate in suspension, is removed by decantation through an opening in the side of the tank at a height flush with the top of the bed of sand tails. The bed of sand remaining in the tank is washed with water or more weak vanadium liquor, and is again stirred to remove any sulphates. The liquor first decanted and the first wash liquors go to a storage tank, while the succeeding wash liquors, being weaker in radium content, go to a second storage tank. These weak liquors are used for first washes on new lots of ore, the sulphates accumulating in this tank being periodically cleaned up and combined with other lots of sulphates.

The liquor and sulphates in the first storage tank are siphoned or pumped to a wooden frame filter press equipped with Duriron pumps. The vanadium-uranium liquor passing through as filtrate is pumped to storage tanks. The first wash waters from this operation are also pumped to this tank, while the remaining part of the wash water, which contains vanadium, is pumped to the storage tanks containing the last washes from the sand tails. When the press cake has been washed, the press is stripped and the cake sampled and weighed. These crude sulphates are transferred to pressure kettles, where water and a calculated excess of sodium carbonate are added, and the mass is 'cooked' under steam pressure until the barium sulphate, together with the radium sulphate, which always follows barium, is converted to the carbonate, with formation of an equivalent amount of sodium sulphate. The contents of the pressure kettles are then pumped through iron-frame filter presses. The frames and cloths used on the filter presses are carefully inspected to make sure that they fit perfectly and that the cloths are free from thin spots or holes. Any leakage would be the cause of losing radium-bearing material of considerable activity. The radium-barium carbonate so obtained is stripped from the presses, sampled and weighed.

The barium-radium carbonate is then dissolved in a tank with dilute, sulphate-free hydrochloric acid. This acid chloride solution, together with the insoluble matter, is pumped through a wooden-frame filter press. The filtrate, together with the first wash waters, is run to a storage tank, while the later, weaker wash water is run to a second storage tank. The chloride liquor in the first tank is treated with sulphuric acid to precipitate the barium-radium chloride present as the sulphate. Samples of the liquor are tested from time to time during the precipitation to ensure an excess of sulphuric acid. If the foregoing operations have been properly conducted the second carbonates will be of sufficient purity, of high activity, and suitable for crystallising.

The carbonates are dissolved in dilute, sulphate-free hydrochloric acid. The acid solution of barium-radium chlorides so obtained is filter pressed through a wooden-frame press. The filtrate from the press goes to a system of large crystallising pots. These pots may be either of acid-proof enamelware or earthenware.

Separation of the radium from the barium by fractional crystallisation is started as soon as the chloride liquor has been sampled. This first liquor is concentrated by boiling until close to the saturation point. It is then allowed to cool. On cooling, crystals of radium-barium chloride will form. These crystals will be richer in radium in proportion to barium than was the original liquor. The mother liquor is removed from the crystals and its volume carefully measured. It is then sampled, and the radium content is determined by the electroscope. The crystals are dissolved in sulphate-free water and hydrochloric acid. The volume of this solution is also measured, a sample taken, and the amount of radium contained determined. The solution of the first fraction crystals is again crystallised, when there will be obtained another crop of crystals richer in radium in proportion to barium than were the first crystals. The first mother liquor is concentrated further, cooled, and another crop of crystals obtained which are weaker in radium than the first fraction, but richer in radium in proportion to barium than was the mother liquor from which they were obtained. These processes are repeated until the mother liquors are practically free from

radium. It is never possible in practice to get the mother liquors free from all traces of radium. The fractional crystallising continually reduces the bulk of the crystals, with a corresponding increase in the amount of radium per pound of barium. When the bulk of the crystals is small enough they are transferred from the pots to a table, where the crystallisation is carried on in large silica dishes. The procedure on the table is exactly the same as in the pots, the only difference being that a smaller volume is handled. As the purity increases with each fractionation, more and more care is required in handling the succeeding fractions, as the loss of a little liquor or a small amount of crystals with their high radium content is a serious matter.

When the fractionation has proceeded to a point of sufficient purity, the chlorides are converted to bromides and the purification by fractional crystallisation is continued. The bromide crystallising is usually carried out in a separate room. Each fraction received from the chloride tables is carefully sampled and analysed. The reason for duplicate determinations on these samples is to avoid even the temptation of theft as well as to supply an accurate record of the work in the two branches of the crystallising laboratory.

The fractions, after sampling, are carefully carbonated with ammonium carbonate, which precipitates the radium and barium as carbonates. The carbonates are separated from the liquid by filtration through suction funnels. The carbonates on the filter are washed with dilute ammonium carbonate solution and then dissolved in hydrobromic acid. This original bromide solution is measured, sampled, and analysed as a check against losses in the conversion process. After sampling, the crystallisation of the bromides is commenced. The crystals of each fraction and also the mother liquors of each fraction are sampled and analysed. When the purity has been carried to a point where the crystals can be handled in small dishes of about 6 ins. diameter, further fractionations are carried out in a water bath. The final fraction is carefully crystallised, the mother liquor is decanted from the crystals, and the crystals are dried to remove all moisture. The radium bromide so obtained is immediately transferred to a small thin-walled glass tube by means of a small metal applicator. The tube is then sealed by drawing to a point in a small gas flame. While transferring the bromide to the tube it is held with forceps and not with the fingers. A radium burn is by all means to be avoided, as, unlike a burn from fire, it continues to attack the flesh, and if at all severe even parts of the finger bones will be destroyed.

The different fractions obtained in the bromide crystallisations are preferably tubed separately, so that a check on the crystallising work may be kept.

The tubed radium is delivered to the electroscopic laboratory for estimation by means of the gamma ray electroscope. Tubed radium, of course, on account of its activity, is never kept in the electroscopic laboratory, but in a safe or vault provided for the purpose and located some distance from the laboratory, the radium being taken in only for estimation and immediately returned. A reading is made on the tube as soon after its delivery by the crystallising laboratory as possible, so that the crystallising laboratory may know the amount tubed in each fraction and be guided in their work. The first reading, made immediately after tubing, is never accepted as anything but approximate. Four days later a second reading is made and recorded, and the final reading is made after thirty days have elapsed since tubing, the radium then being in equilibrium with its emanation and the results accurate and final.

The vanadium-uranium liquors in the storage tanks, from which the sulphates have been removed, are allowed to collect until the tanks are nearly full. Sodium carbonate is added until the liquid is but slightly acid, then sodium nitrite is added, and the tank is heated to boiling by steam. If the liquid is but slightly acid at this time, the vanadium oxide, carrying some iron and uranium and considerable amounts of soda salts, will be precipitated. The precipitation is never complete, but if the acidity is checked by volumetric control tests during the process a very good recovery is obtained. The precipitate will be granular in character and will filter readily. When the reaction has been completed the vanadium oxide is separated by filter pressing. The cake is analysed for moisture and vanadium oxide. The vanadium oxide so precipitated finds a ready market with manufacturers of ferro-alloys.

If it is desired to recover the uranium oxide remaining in the filtrate from the precipitation of the vanadium oxide it is returned to tanks for the purpose, and the uranium precipitated as sodium uranate by addition of sodium hydroxide until the liquor is alkaline. The sodium uranate so precipitated will carry the rest of the iron in the solution and also the major portion of the unprecipitated vanadium.

Extraction from pitchblende.—The crushed mineral, after a preliminary roasting in air, is heated with sodium carbonate in a reverberatory furnace. The product is washed with water and then with dilute sulphuric acid, to remove the uranium as soluble uranyl sulphate. All the radium is left in the insoluble residue, which consists mainly of lead and calcium sulphates, silica, alumina, and ferric oxide, but which contains small amounts of copper, bismuth, zinc, cobalt, manganese, nickel, vanadium, antimony, thallium, rare earths, niobium, tantalum, arsenic, &c. The original method of working up these residues, due to Debierne, is as follows :

The residue is boiled with concentrated sodium hydroxide solution, to remove most of the lead sulphate, silica, and alumina, and the insoluble portion well washed. This is then attacked with hydrochloric acid, in which a large proportion dissolves. The radium is left in the insoluble portion, which is washed, again treated with sodium hydroxide, and the insoluble residue vigorously boiled with concentrated sodium carbonate solution to convert barium and radium sulphates into carbonates. The solid is filtered off, washed with sodium carbonate solution and then with water, and dissolved in hydrochloric acid. The filtered ehloride solution is treated with sulphuric acid

to precipitate radium and barium sulphates, which are contaminated with traces of lead and calcium sulphates. The sulphates are again converted into carbonates and then into chlorides. The acid chloride solution is treated with hydrogen sulphide, and the precipitate, which contains polonium, is removed. The filtrate is oxidised and treated with ammonia, when a precipitate is removed containing actinium. From the filtrate, radium and barium carbonates are thrown down, and the washed precipitate converted into chlorides. The solid chlorides are washed with concentrated hydrochloric acid to remove traces of calcium chloride, and the residual radium and barium chlorides are then separated by fractional crystallisation. This is effected at first from aqueous solution, but in the later stages, when the quantity of material containing radium has been largely reduced, solutions in hydrochloric acid of gradually increasing strength are used as solvent, since the solubility of the chlorides is thereby largely diminished. The final crystallisations are made from the most concentrated acid that can be prepared by distillation. Radium chloride, being less soluble than barium chloride, accumulates in the less soluble fractions (Mme. Curie, Translation of Thesis for Doctorate, Chem. News, 1903, 88, 85).

If hydrogen chloride is led into mixtures of barium and radium chlorides till precipitation begins, the first fractions precipitated are richer in radium than the later ores; and practieally the whole of the radium is precipitated with the first two-thirds of the barium chloride (Ebler and Bender, Ber. 1913, 46, 1571).

A similar method of treatment, employed on a large scale by Haitinger and Ulrich (Monatsh. 1908, 29, 485; *cf.* Paweck, Zeitsch. Elektrochem. 1908, 14, 619), has been more fully described. The residue is originally boiled with half its weight of sodium hydroxide (25 p.c. solution), the insoluble portion treated with one and a half times its weight of hydrochloric acid (1 : 1), and the solid residue boiled with half its weight of sodium carbonate (25 p.c. solution). This treatment with sodium carbonate is performed three times, to ensure the conversion of all the radium into carbonate. The subsequent treatment is essentially that already described.

One ton of Joachimsthal residues yields from 10 to 20 kilos. of the crude barium-radium sulphate mixture having an activity about sixty times that of uranium. A careful examination of the radium in all the by-products from the extraction of radium from 10 tons of Joachimsthal pitchblende, showed that there are present in all only 0·26 grm. of which two-thirds was present in the unattacked residue from the soda extractions, and about one-quarter in the lead products (H. Souczek, Sitzungsber. K. Akad. Wiss. Wien, 1910, 119, [ii. *a*] 371).

The radium-barium sulphate mixture may with advantage be reduced to sulphide by ignition with carbon or with calcium carbide or hydride (Ebler and Bender), or in a current of coal gas, and then dissolved in hydrochloric acid (Soddy). The chlorides of radium and barium may be almost quantitatively precipitated from aqueous solution by saturating with hydrogen chloride.

The fractionation of the mixed *bromides* of radium and barium is said to be more rapid, but less regular, than that of the chlorides (Giesel, Ann. Chim. 1899, [ii.] 69, 91; Ber. 1902, 35, 3608; Scholl, J. Amer. Chem. Soc. 1920, 42, 889). For another method of separating radium and barium, *v.* Marckwald, Ber. 1904, 37, 88.

Extraction from monazite sand.—Brazilian monazite sand containing 6·54 p.c. of thoria and $8{\cdot}21 \times 10^{-10}$ grams of radium per gram is decomposed by heating it with twice its weight of strong sulphuric acid and 0·2 p.c. of barium chloride crystals in cast-iron pots. The cooled mass is dissolved in 10 parts of water and the slimy material washed away from undecomposed sand by decantation, hydrochloric acid being added from time to time to prevent precipitation of thorium phosphate. The black slimes in the decanted liquor are allowed to settle and separated by decantation; they contain over 90 p.c. of the barium added and 65 p.c. of the mesothorium present, together with up to 20 p.c. of lead compounds and much graphite from the pots. By repeated washings with hot water much of the lead chloride is removed, and the residue then contains 15 p.c. of lead sulphate and about 50 p.c. of barium sulphate, as well as about 1 mg. of radium and mesothorium per kg. Three methods of working up this residue gave good results; they were: (1) heating with carbon in iron pots and solution of the sulphides in hydrochloric acid; (2) fusion with sodium carbonate, extraction of the mass with water, and solution of the residue in hydrochloric acid; (3) prolonged boiling with a concentrated solution of sodium carbonate, followed by treatment of the residue as in (2). Digestion of the slimes with six times their weight of concentrated sulphuric acid, followed by filtration of the hot acid through asbestos and subsequent dilution with water gave a pure lead-barium sulphate containing all the radium and mesothorium, so that this preliminary treatment was adopted previous to the conversion into chlorides described above. In all cases the lead-barium chloride solution was made just alkaline with ammonia and saturated with hydrogen sulphide to remove lead; the filtrate was then subjected to fractional crystallisation to recover the radium and mesothorium. Throughout the work careful analytical checks of the radium content were made by the emanation method owing to the difficulty of determining mesothorium by the gamma ray method (H. Schlundt, U.S. Bureau of Mines, Chem. News, 1923, 127, 139–141, 153–155; J. Soc. Chem. Ind. 1923, 42, 974 A.).

Radium accidentally dropped may be recovered by evaporating the sweepings and washings of the pavement in a water-bath, mixing and fusing the residue with a mixture of 2 pts. of sodium carbonate, 2 pts. of potassium carbonate, and 1 pt. of sodium nitrate, and lixiviating the cooled mass with hot water. The radium is thus brought into solution, and is then completely recovered by the precipitation in the liquid of barium sulphate which carries down the radium with it (W. Cialdea, Gazz. chim. ital. 1923, 53, 42; J. Soc. Chem. Ind., April 27, 1923, 352A).

For methods of concentrating the radium in the barium-radium chloride mixture depending

on adsorption and deabsorption, *v.* Ebler and Bender, Zeitsch. angew. Chem. 1915, 28, 25.

Extraction from minerals of the titano-niobate type.—The difficulty of obtaining a solution containing the constituents of minerals of the titano-niobate type has led to the following method. The ground mineral is treated with hydrofluoric acid, the product being evaporated to dryness, and fused with potassium hydrogen sulphate until sulphur trioxide vapours are no longer evolved. The cooled melt is mixed with sodium sulphate or even with lithium sulphate as well, to obtain a minimum melting-point, the whole is heated to redness, cooled, broken into pieces, and then transferred to a Pyrex glass tube. By heating to 500°–600°, the product becomes completely liquid, and the radium content may be determined in the usual way, the emanation being displaced by using a current of air, passed over soda-lime heated at 150° to remove acid fumes, and then measured (A. Karl and S. Lombard, Compt. rend. 1923, 177, 1036–1037; J. Soc. Chem. Ind. 1924, 43, B. 15).

The world's stock of pure radium in 1922 was estimated at from 100 to 110 grms., of which about 70 grms. was extracted in the United States from the carnotite deposits in Colorado and Utah and much of the remainder from Mexican ores. The supply in the United States for therapeutic use was about 20 to 25 grms. According to Rutherford Europe had produced about 40 grms. of radium and America 120 to 130 grms. up to 1922. Its commercial price in 1922 was £20,000 per grm. The production at Joachimsthal was said to be 1·1 grms. in 1919, 2·2 grms. in 1920, and 3·2 grms. in 1921. The Czecho-Slovakian government reserves the exclusive right of exploiting all radium ores in the country.

According to the Chemical Trade Journal, August 31st, 1923, it is not generally realised how completely the world's radium position has changed since the discovery in 1913 of new sources of uranium ore in the Belgian Congo, and particularly since the discovery of the Kasolo deposit by the British prospector, Sharp, in 1915. Up to within a year or two ago—for the outbreak of war did not permit extensive work on the Congo deposits till 1919—by far the greater proportion of the world's radium had been derived from the deposits of Colorado and Utah, which yield about 5 mgs. of radium per ton, and in all some 160 grms. of radium bromide had been produced. The new Belgian deposits, however, have proved so rich in radioactive constituents (about 150 mgs. per ton), and comparatively so easy to work, that the American producers have found the competition too severe and have decided to close down their mines for some years to come. The Belgium mineral is worked up at Ooleu, near Antwerp, where the largest and most up-to-date plant in the world has been erected and put into full operation within the short space of eighteen months. The method of extraction employed at Ooleu does not differ materially from that worked out by Curie and Debierne. Uranium, iron, copper, lead, calcium, and phosphoric acid are eliminated by a series of operations which leave, as the final product, barium chloride, containing about one part in 125,000 of radium chloride. The two chlorides are separated by an exceedingly lengthy series of fractional crystallisations, the first sixty of which are effected in enamelled cast-iron pans of continuously decreasing dimensions, and the subsequent fractionations are carried out in the laboratory until some 2 to 3 grms. of highly radioactive product is obtained. The material is then freed from any trace of lead by hydrogen sulphide, the chlorides converted into bromides, and the operation of crystallisation continued until a product containing 95 to 96 p.c. of radium bromide is reached. Six months ago the current price of radium in the world's markets was £20 to £25 per mg. At present the Belgian company, the Société Générale Métallurgique, is offering radium in unlimited quantities at £14 per mg., and the price can certainly still further be reduced. The Ooleu works are now producing 3 grms. of radium per month, and this production can be increased, if necessary, to 6 grms., which means a yearly output of 36 to 72 grms. Cheap and plentiful supplies of radium, which leave a considerable surplus after medical and purely scientific needs have been met, must lead inevitably to new and valuable industrial applications being found for the material, and it is far from impossible that, in the domain of organic chemistry at least, radium may be found an effective catalyst for carrying out certain reactions which at present require high pressures and temperatures, under more comfortable conditions (Pharm. J., September 22nd, 1923).

Preparation of radium.—About 0·1 grm. of pure radium chloride was electrolysed in solution with a mercury cathode. The fluid radium amalgam was dried and carefully heated in an iron boat in a current of pure hydrogen under reduced pressure. At 400°, the amalgam became solid; no more mercury was evolved at 700°, and metallic radium was left in the boat (Mme. Curie and Debierne, Compt. rend. 1910, 151, 523). A metallic mirror, apparently containing radium, has been obtained by heating its azoimide $Ra(N_3)_2$ at 185°–250° in a vacuum (Ebler, Ber. 1910, 43, 2613).

Properties.—Radium is a brilliant, white metal, which melts sharply at about 700° and volatilises appreciably at that temperature. It adheres strongly to iron. It tarnishes rapidly in the air, forming a nitride, and vigorously decomposes water with evolution of hydrogen, forming radium hydroxide solution.

Radium compounds closely resemble those of the alkaline earth metals, and particularly those of barium, with which they are isomorphous. The volatility of the bromides of calcium, strontium, barium, and radium diminishes in the order given (Stock and Heynemann, Ber. 1909, 42, 4088); but so far as the volatility of the elements is concerned, radium resembles calcium rather than barium. The physical and chemical properties of the compounds of the alkali and alkali earth metals usually show a well-marked gradation in the order—calcium, lithium, strontium, barium, sodium, potassium, rubidium and cæsium, and in this scheme radium comes between barium and sodium (de Forcrand, Compt. rend. 1911, 152, 66).

The *chloride*, *bromide*, *nitrate*, *carbonate*, *sulphate*, *azoimide* and *platinocyanide* of radium are known. The salts are colourless when freshly

prepared, but develop colour on standing; they are luminous in the dark, and continuously evolve heat at the rate of 118 calories per hour per grm. of radium (Schweidler and Hess, Monatsh. 1908, 29, 853; *cf.* Curie and Laborde, Compt. rend. 1903, 136, 673; Rutherford and Barnes, Phil. Mag. 1904, 7, 202).

The *chloride*, which is hygroscopic, closely resembles barium chloride; in preparing it in the pure state, care must be taken to eliminate the trace of lead chloride which is invariably present. Radium chloride is para-magnetic (Curie and Cheneveau, Soc. franç. de phys. 1903). The *bromide* is an unstable substance, losing bromine on keeping and passing into the hydroxide, and eventually, by absorption of carbon dioxide, into the carbonate (Giesel, *l.c.*; Ramsay, Monatsh. 1908, 29, 1013; Thorpe, *v. infra*). It has been observed to explode in contact with water (Jost, Chem. Zeit. 1912, 36, 138). The freshly prepared anhydrous bromide has a beautiful blue fluorescence. The crystals of the bromide have been measured by Rinne (Centr. Bl. f. Min. u. Geol. 1903, 134). *Radium sulphate* is the least soluble sulphate known. For the conditions determining its solubility, *see* Lind, Underwood and Whittemore, J. Amer. Chem. Soc. 1918, 40, 465. For other salts, *see* Merck and Eichholz, D. R. P. 256666.

Radium salts and solutions colour glass and rock crystal a deep purple, fluorspar becomes blue, selenite brown. The colours are discharged on heating but may be restored on exposure to the γ-rays of radium (Newbery and Lupton, Mem. Manchester Phil. Soc. 1918).

The effect of rays from radium on soda-lime glasses has been studied by Clarke (J. Soc. Glass Technology, 1921, 5, 155). All glasses containing selenium or cobalt oxide are coloured brown by β-rays, the depth of coloration corresponding with the range of the β-particles in the glasses. The intensity of coloration is greatest at the surface, decreases towards the interior, and increases with the amount of selenium or cobalt oxide present. Pure soda-lime glass is only affected by α-rays and is faintly coloured on the surface only. All kinds of glass fluoresce in radium emanation, but the fatigue effect is observed at about the same time as the attainment of maximum intensity of coloration. The coloration of glasses is probably due to the formation of colloidal particles in the glass, owing to the action of α- or β-rays on ions already present in the glass. The fluorescence is held to be due to mechanical bombardment of the glass molecules by the rays. Nineteen different kinds of glass were examined, five of these were coloured purple and fourteen brown; it was found that the former contained manganese, whilst the latter did not (J. R. Clarke, Phil. Mag. 1923, 45, 735).

Direct (probably α) radiation is necessary to colour the diamond. Colouring is not produced by the penetrating (β- and γ-) radiation from radium salt contained in glass tubes, 0·5 to 1 mm. thick. Green coloration is always produced by direct radiation either from high-grade radium salts or from radium emanation. The green colour is not destroyed either by diffused or by direct sunlight, but can be removed by heating the diamond to a dull red heat for half an hour or less. Similarly the green colour is removed by re-cutting the crystal, a result probably due to the heat produced in the cutting process. Radiation from the emanation is more effective than that from the salt in the production of colour, owing to the greater absorption of α-rays by the salt. In some cases of colouring by the emanation, black spots, consisting probably of a form of carbon, were formed in the interior of the diamonds employed. These 'carbon spots' occurred beyond the range of α-rays in the crystals, and it is suggested that they and the colouring are attributable to some form of secondary radiation more penetrating than α-rays. Prolonged exposure in air to a red-heat caused the 'carbon spots' to disappear permanently (S. C. Lind and D. C. Bardwell, J. Franklin Inst. 1923, 196, 521–528; J. Soc. Chem. Ind. 1923, 42, 1130 A.).

The ionic mobility of the radium ion is 57·4 ($\frac{1}{2}$Ra). For the electrochemical behaviour of radium, *v.* Coehn, Ber. 1904, 37, 811.

For disintegration of radium and allied elements, *see* article Radiology. On the relation between uranium and radium, *v.* Soddy and Hitchins, Phil. Mag. 1915, [vi.] 30, 209; Soddy, *ibid.* 1919, [vi.] 38, 483.

Spectrum.—Radium salts colour the flame a pure carmine-red; the flame spectrum shows four bands in the red and one in the blue. The spark spectrum has been studied by Demarçay (Compt. rend. 1898, 127, 1218), Runge (Ann. Physik. 1903, 10, 407), Exner and Haschek (Wien. Ber. 1901, July 4), Runge and Precht (Ann. Physik. 1904, 14, 418), and Crookes (Proc. Roy. Soc. 1904, 72, 295). High frequency spectrum, *v.* Siegbahn and Friman, Physikal. Zeitsch. 1916, 17, 61. The most intense lines in the spark spectrum are 4683, 4436, 4341, 3814, 3650, 2814, 2709, and of those occurring in the photographic region of the spectrum, the strongest line is 3814, in the ultraviolet. The relative intensities of the two neighbouring lines, 4553·3 (radium) and 4554·2 (barium), furnishes a good test of the completeness of the separation of the two elements. The barium line is seen with the same intensity as the radium line when only 0·6 p.c. barium is present in a radium salt. A more stringent test (Huggins) is to compare the intensity of the line 5536·2 (Ba) with that of the lines 5813·8 and 5560·8 (Ra).

Atomic weight.—The analogy between radium and the alkaline earth metals, and the isomorphism of radium and barium salts, show that radium is a divalent metal, and its atomic weight is therefore twice its chemical equivalent (*cf.* Freundlich and von Elissafoff, Physikal. Zeitsch. 1913, 14, 1052). The first determinations, made on about 90 mgms. of radium chloride, gave the value 225 for the atomic weight (Mme. Curie, Ann. Chim. 1903, 30, 99), while later analyses of 0·4 grm. of the chloride, gave the value 226·2 as the mean of three concordant experiments (Mme. Curie, Compt. rend. 1907, 145, 422). This value was confirmed by Thorpe (Proc. Roy. Soc. 1908, 80 A, 298; Chem. News, 1908, 97, 229), who found the value 227 by the analysis of 60 to 80 mgms. of the chloride. Hönigschmid (Sitzungsber. K Acad. Wiss. Wien, 1911, 120, [ii.*a*] 1), working with a gram of highly purified radium chloride, found for the ratio $RaCl_2$: AgCl the value 1·03554, whence Ra=225·95,

and for the ratio $RaCl_2 : 2Ag$, the value 1·37592, whence Ra=225·96. Another series of determinations (*l.c.* 1912, 121, [ii.*a*] 1) using radium bromide gave 225·97 (Ag=107·88). The most probable value is therefore 226. Gray and Ramsay (Proc. Roy. Soc. 1912, 86, A, 270) by converting the bromide into chloride and *vice versâ* have obtained the value Ra=226·36.

Runge and Precht calculated the value 257·8 for the atomic weight of radium, from spectroscopic considerations (Phil. Mag. 1903, [vi.] 5, 476); but according to Watts, their calculation, which involves an extrapolation, is only approximate, and when carried out more exactly, yields the value 226·6 (Watts, *ibid.* 1903, [vi.] 6, 64; 1909, [vi.] 18, 411), in good agreement with the chemical value.

Estimation of radium: chemically.—The estimation of radium in a mixture of radium and barium salts can be effected by ordinary indirect analysis, *e.g.* determination of the weight of the mixed chlorides and the percentage of chlorine in the mixture. This method is only available when the radium forms an appreciable percentage of the mixture.

Physically.—(i.) By measurement of its γ-radiation. A standard preparation of known radium content is required. The preparation to be examined must have been prepared at least a month, and preferably kept in a sealed tube, since the γ-radiation is due to the disintegration products formed from radium. A large lead electroscope is employed, provided with a single gold leaf insulated by a sulphur bead. The rate of leak is determined for a weight w_1 of the material under examination and a weight w_2 of standard substance. Call these rates r_1 and r_2 scale divisions per minute respectively. The calculation may be illustrated with reference to the examination of a pitchblende for radium, supposing that the standard employed was a pitchblende containing p p.c. of uranium. The percentage x of uranium in the substance is given by

$$x = \frac{w_2}{w_1} \times \frac{r_1}{r_2} \times p = q \text{ say}$$

and from the 'equilibrium ratio' the amount of radium is given by $0{\cdot}01q \times 0{\cdot}32 = 0{\cdot}0032q$ grms. radium per ton of material.

From 20 to 100 grms. of a pitchblende should be taken, according to its richness; larger quantities of other substances, if poorer in radium, must be used.

In the presence of thorium, this method gives results too high, owing to the penetrating γ-radiation of mesothorium being measured as well. This may be allowed for in the case of a preparation that can be dissolved and the solution evaporated to dryness, for the radium emanation escapes, and three hours afterwards the γ-activity is that due to the mesothorium alone (*cf.* Bothe, Physikal. Zeitsch. 1915, 16, 33; Lind, J. Ind. Eng. Chem. 1915, 7, 406).

(ii.) The Emanation method. Solutions containing from 10^{-8} to 10^{-10} grms. of radium may be acidified, sealed up in a small distilling flask and the radium emanation allowed to accumulate for a month, when the equilibrium amount is present. The emanation is then boiled out of the solution in a slow stream of air, and the air dried and passed into an exhausted electroscope. The leak, 3 hours after admission, is measured. Comparison with a standard substance in a similar flask is necessary (Lloyd, J. Phys. Chem. 1910, 14, 476; Mme. Curie, Le Radium, 1910, 7, 65; *cf.* also *ibid.* 1909, 6, 195; Lind, J. Ind. Eng. Chem. 1915, 7, 1024; Barker, *ibid.* 1918, 10, 525).

A new method of determining the radium content of carnotite ores and other products of low activity has been described by V. F. Hess (Am. Electrochem. Soc. Trans. 41, 287–301; Disc. 301–302, 1922). When carnotite or other materials are filled into the space between two concentric spheres, the gamma-ray effect in the centre of the inner sphere can be calculated. This formula was taken as a basis of a direct method of determining the radium content of these substances. The samples were filled in wooden containers which were closed hermetically. The gamma-ray electrometer was introduced into the centre. The observed ionisation, expressed in absolute units (E.S.U.) reduced by certain constants, gives directly the radium content per gram of material. The method is sensitive enough to give correct figures for material with 10^{-10} gram of radium per gram of material. It is very simple, and requires no chemical treatment of the samples before the measurements. The results on ore samples were compared with the results derived from the chemical analysis of the uranium content, and were found to be in good agreement (Sci. Absts. 1923, 26, 644). *See* also C. E. Baumgarten and H. H. Barker (J. Ind. Eng. Chem. 1923, 15, 597–599).

For a method of examining radium residues containing actinium, *see* Auer von Welsbach, J. Soc. Chem. Ind. 1911, 30, 535.

For the radioactive properties of radium and its compounds, *v.* RADIOLOGY.

For the recovery of radium from luminous paint, *see* A. G. Francis, J. Soc. Chem. Ind. 1922, 41, 94 T.

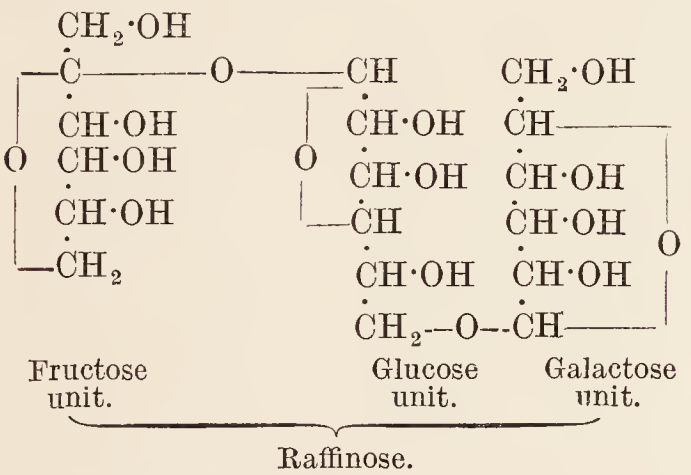
For the transformation of radium, *see* Rutherford (J. Soc. Chem. Ind. 1911, 30, 659). Radium constants on the international standard, according to Rutherford (Phil. Mag. 1914, 28, 320), are as follows: The equilibrium ratio of radium to uranium is $3{\cdot}23 \times 10^{-7}$; the yearly production of helium per gram of radium 164 cu. mm.; the total observed heating effect per gram of radium in equilibrium with its first four products is 134·7 calories per hour, made up of radium 25·1, emanation (niton) 28·6, radium A 30·5, B and C 50·5; the equilibrium volume of emanation per gram of radium 0·63 cu. mm.; number of α-particles expelled per second per gram of radium, itself, $3{\cdot}57 \times 10^{-10}$, in equilibrium with first four products $14{\cdot}3 \times 10^{-10}$; the total positive charge in the latter case, 33·2 E.S.U., or $1{\cdot}11 \times 10^{-9}$ E.M.U.; the total negative charge carried by the β-particles of radium B and C, 18·3 E.S.U.; the total saturation current due to α-rays from 1 curie of emanation, itself, $2{\cdot}89 \times 10^6$ E.S.U., and with its products, $9{\cdot}94 \times 10^6$.

According to the *Czechoslovak Trade Journal*, roughly 24 grms. of radium, or about 12 p.c. of the world's output, was produced at Joachimsthal during the years 1909–22. It is estimated that the total world's production of radium to date is about 204 grms. Production in Czecho-

slovakia in 1920 was 2·2 grms. (valued at 22 million kronen); in 1921, 3·2 grms. (32 mill. kr.); and in 1922, 2·2 grms. (11 mill. kr.) (J. Soc. Chem. Ind. 1924, 43, 203).

RAFFINOSE, MELITOSE, *v.* CARBOHYDRATES.

Raffinose, prepared from cotton-seed meal, gives rise on methylation to hendecamethyl raffinose distilling at 238°–240°/0·02 mm., and showing $[\alpha]_D$ +128°. Hydrolysis of this product with 1 p.c. hydrochloric acid at 90°C. leads to the isolation of three partly methylated hexoses, which were recognised respectively as tetramethyl γ-fructose, identical with that isolated from methylated sucrose, as 2 : 3 : 5-trimethyl glucose (butylene oxidic), which gave a crystalline methylglucoside melting at 74°C., and as a tetramethyl galactose, which gave a crystalline anilide identical with that prepared from methylated lactose. From a constitutional study of these cleavage products the following structural formula for raffinose is deduced :—



Raffinose.

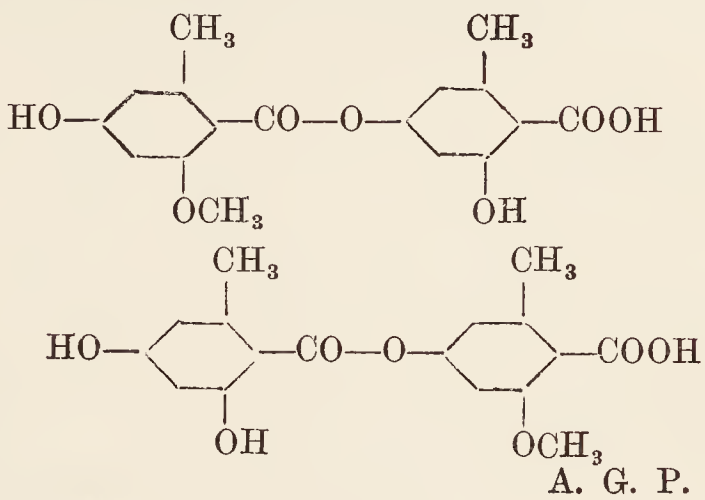
It would therefore appear that the constitution of melibiose is to be represented by a formula in which the glucose unit, through the hydroxyl group attached to its terminal carbon atom 6, is linked with the reducing group of galactose (W. N. Haworth, E. L. Hirst, and D. A. Ruell, J. Soc. Chem. Ind. 1923, 42, 1139; Chem. Soc. Trans. 1923, 123, 3125).

RAISIN SEED OIL. Californian raisin seed oil is of light amber colour and has the following characters: iodine value (Hanus), 125·8; (Wijs), 128·0; saponif. value, 196·4; n^{25}=1·4720; acid value, 12·6. When mixed with 5 p.c. of liquid drier (U.S. Government specification) a fairly firm film is formed in 14 hrs., but this remains tacky for 8 days. With 10 p.c. of liquid drier the tackiness is somewhat greater. The films are in both cases better than films obtained with raw soya bean oil similarly treated. Paints made up with raisin seed oil containing 5 p.c. and 10 p.c. of drier, using lead or zinc oxide as pigment, dried to a fairly firm film in 12 hours, but remained tacky as before. The results were again superior to those obtained with soya bean oil. A slight pinkish tinge developed in white paints about 8 days after drying. It would therefore appear that, while not satisfactory when used alone, raisin seed oil could be used in conjunction with linseed oil, in the manufacture of paint liquids (H. A. Gardner, Circ. No. 190, U.S. Paint Manuf. Assoc., Oct. 1923; J. Soc. Chem. Ind. 1923, 42, 1138 A).

RAMALIC ACID (lecanoric acid monomethyl ether), $C_{16}H_{13}O_6.OMe$, has been isolated by Hesse by means of ether, from the lichens *Ramalin pollinaria* (J. pr. Chem. [i.] 57, 253) and *Evernia divaricata* (Ber. 1897, 30, 357). It crystallises in colourless needles, m.p. 179°–180°C., and gives with alcoholic ferric chloride a violet coloration. It differs from the isomeric evernic acid, which occurs in conjunction with it, in being sparingly soluble in ether (Zopf, Annalen, 297, 306), but when hydrolysed with baryta water behaves like evernic acid, producing orcin, carbon dioxide, and everninic acid (*cf.* EVERNIC ACID).

The anhydrous potassium and barium salts, the latter of which is sparingly soluble, have been prepared and described by Hesse (J. pr. Chem., 1898, [ii.] 57, 232).

The structure of ramalic acid is represented by one of the following formulæ :—



or

A. G. P.

RAMIE *v.* CHINA GRASS.

RAMMELSBERGITE. Nickel diarsenide, $NiAs_2$, crystallised in the orthorhombic system and dimorphous with the cubic chloanthite (*q.v.*). The nickel may be partly replaced isomorphously by cobalt and iron. The colour is tin-white with a reddish tinge on the fresh fracture. Sp.gr. 7·1–7·2, H. 5½–6. The mineral occurs in veins at Schneeberg, Marienberg and Annaberg in Saxony, Eisleben in Thuringia, Riechelsdorf in Hesse, &c. L. J. S.

RAPE, *Brassica Napus oleifera* (DC.). Winter rape, a plant grown largely for the sake of its seeds which are rich in oil (*v.* RAPE OIL); also to some extent as forage for sheep and as a catch crop. Summer rape, or colza, is another variety, *Brassica Napus annua* (Koch).

According to König, the seeds contain, on the average—

Water	Protein	Fat	N-free extract	Fibre	Ash
7·3	19·6	42·2	20·8	6·0	4·2

The seeds, and indeed the whole plant, contains a pungent volatile oil—a mustard oil—which is not identical with allyl thiocarbimide and is less poisonous than that substance (Sjollema, Landw. Versuchs. Stat. 1900, 54, 311). It is, however, hurtful to animals, and the use of rape cake—left after expression of the oil from the seeds—as a food for cattle not infrequently causes death (Jörgensen, Bied. Zentr. 1898, 27, 697). According to Jörgensen (Landw. Versuchs. Stat. 1899, 52, 269; *ibid.* 1910, 72, 1), the thiosinamine from rape cake always contains less nitrogen than corresponds with the allyl compound (24·24 p.c.), and the higher the percentage of nitrogen in the thiosinamine from the cake, the more pungent is the odour and the more poisonous the cake. He concludes that if a cake yields, on treatment for an hour with white mustard (to supply the enzyme, emulsin), more than 0·5–0·6 p.c. of

mustard oil, and if the thiosinamine obtained from the mustard oil contains more than 22 p.c. of nitrogen, there is danger of the cake being poisonous to cattle. Moreover, the pungent taste of the cake renders it unpalatable, and in England it is seldom used as a food, but is employed as a manure, cheifly for the sake of the nitrogen (about 5–6 p.c.) which it contains. It is a slow-acting manure.

Green rape, before or during flowering, forms a useful food for sheep. According to Kellner, winter rape, in flower, contains—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
85·9	2·8	0·8	5·7	3·5	1·3

Of the total protein, 1·3 p.c. is digestible proteids. It is occasionally made into hay, which, according to Kellner, has the composition—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
15·5	15·7	4·4	34·6	20·5	9·4

Of the protein, 8·5 p.c. is digestible proteids.

H. I.

RAPE OIL (COLZA OIL). The various kinds of rape oil are obtained from the seeds of *Brassica campestris* and of several largely cultivated varieties of the species, belonging to the natural order *Cruciferæ*. The oils from these plants are, especially in this country, indiscriminately termed rape oil or colza oil; on the Continent, however, two different kinds of oil are understood under the last two names. According to the variety of the plant from which the seed is derived, the following oils may be broadly differentiated:—

1. Rape oil (*Huile de navette ; Rapsoel, Repsoel*), from the seeds of *Brassica napus* (Linn.).

2. Rübsen oil (*Huile de rabette ; Ruebeol, Rubesenoel*), from the seeds of *Brassica campestris B. rapa*, Linn.).

Both Brassica species furnish several, by no means sharply distinguished, varieties, which are again divided, according to the season of the year, into several forms (*see* Lewkowitsch).

Rape seed is grown in almost all European countries. In France and in Belgium the winter variety of *Brassica napus* is chiefly cultivated. Enormous quantities are grown in East India. The bulk of the East Indian seed is imported into England from Calcutta, Madras, Bombay (Guzerat and Ferozepore).

Rape seed is crushed between rollers, and the meal is either expressed or extracted with carbon disulphide or petroleum spirit. The extracted oil is, as a rule, purer than the expressed oil, since a considerable amount of mucilaginous matter passes into the oil when the seed is expressed. The cakes obtained by expression form an excellent cattle food, if the seed has been tolerably pure, *i.e.* free from mustard seeds and wild seeds. The extracted meal is unsuitable as cattle food, and is chiefly used as manure, at any rate in this country, although some meal, especially on the Continent, finds its way into compound cakes.

Rape (colza) seed contains from 33 to 43 p.c. of oil. The seed harvested in the north of France contains 43–45 p.c.; Danubian seed 38–40, and Indian seed from 42 to 45 p.c.

The crude oil is dark in colour, and before being put on the market, it is refined by treatment at the ordinary temperature with about 1 p.c. of strong sulphuric acid (Thenard's process), which coagulates and carries down the impurities. The clarified oil is then washed with water until free from mineral acid.

The refined oil of commerce is pale yellow; it possesses a characteristic smell (which may serve to identify the oil), and except for the finest qualities, an unpleasant harsh taste. It has the following characters: sp.gr. 0·9147 at 15°/4°; $n_D^{20}=1{\cdot}4734$; acid value 1·6; Reichert-Wollny value 0·17; sapon. value 172·8; acetyl value 1·49; iodine value (Wijs) 102·8; unsapon. matter 0·98 p.c. The main constituent of the fatty acids of the oil is erucic acid (65 p.c.) together with some linolic and linolenic acids. The quantity of saturated acids is less than 2 p.c.; they consist of palmitic, stearic, behenic, lignoceric, and arachidic acids (Toyama, J. Chem. Ind. Japan, 1922, 25, 1044). A qualitative test for rape oil has been based by Thomas and Yu (J. Amer. Chem. Soc. 1923, 45, 129) upon the relative insolubility of magnesium erucate in 90 p.c. alcohol. The insoluble soap is recrystallised from alcohol, and the erucic acid afterwards liberated and examined. It melts at about 35° and has an iodine value of about 72. It should be mentioned that magnesium arachidate and elæostearate are also insoluble in 90 p.c. alcohol, so that the test is not applicable in the presence of arachis or tung oil. The term 'colza oil' can no longer be taken as referring to the special oil expressed from the finest French seed as was the case about fifty years ago. For as the consumption of colza oil extended, the seeds from other countries were used for the manufacture of 'colza oil,' especially German seed, such as Rübsen seed from *Brassica campestris* (*B. rapa*). Since Indian rape seed is being refined in large quantities, the term 'colza oil' has become a generic term, denoting a fine rape oil from various kinds of rape seed. Therefore the restriction of 'colza oil' to a French oil or even a German oil no longer holds good, and 'colza' oils are sold in trade which are made from Indian seed, such as Cawnpore seed and Guzerat seed. It should be noted that 'colza oil' was originally an oil which had been obtained by expression, and the term 'best refined colza oil' must still be held as rightly belonging to an expressed oil, such as is used for edible purposes. This class of edible rape oil is largely used by bakers for greasing the ends of loaves in the oven ('bread oil').

There are also in commerce pure refined colza oils which have been obtained by extraction with solvents. These are of distinctly inferior quality, and their taste reveals their origin immediately. Colza oils of this class are not objectionable as burning oils, but being, as stated already, of a distinctly inferior quality, they are valued in the trade at a lower figure.

Jamba oils approximate to rape oils as regards quality; as these jamba oils are now coming in larger quantities on the market, the distinction between rape oils and jamba oils has gained some importance.

Owing to the high molecular weight of erucic acid, the saponification value of rape oil is lower than in the majority of fatty acids

(*see* OILS, FIXED, AND FATS). On treatment with bromine rape oil yields about 1 p.c. of an ether-insoluble bromide, whilst the fatty acids yield 3–4 p.c. of an insoluble bromide (m.p. 179°). For the chemical and physical characteristics, *see* tables under OILS, FIXED, AND FATS.

The ' cold drawn ' oil is used as an edible oil, especially in India. It is also used as an edible oil on the Continent, and in this country as ' bread oil.' The various qualities of refined oil have been mentioned above. Those colza oils, which are unsuitable for edible purposes, find an outlet as excellent burning oils. Equally well-refined oils can also be used as ' wool oils.' Enormous quantities of the oil are used for lubricating purposes, both in the refined state and as ' blown rape ' oil. Smaller quantities are used on the Continent for the making of soft soap. Rape oil is further largely used for quenching steel plates.

When rape oil is passed over a copper-aluminium catalyst at 550°–650°, and the lighter liquid fractions are hydrogenated over reduced nickel at 180°, a mixture of aromatic and cyclic hydrocarbons is obtained, the relative proportions of which vary with the activity of the nickel (Mailhe, Compt. rend. 1921, 173, 658).

J. L.

RAPHIA WAX *v.* WAXES.

RASPBERRY, *Rubus Idaeus* (Linn.). According to König, the fruit contains—

Water	Protein	Free acid, malic	Invert sugar	Cane sugar	Other N-free extract	Fibre and seeds	Ash
85·0	1·4	1·5	3·4	0·9	1·0	6·4	0·5

The odour and flavour of raspberries are apparently due to an essential oil, which has a sp.gr. of 0·8863 at 15°, saponification value 193, is dextro-rotatory and soluble in 30 parts of 80 p.c. alcohol (Haensel's Report, Oct. 1904).

The free acid in the juice contains tartaric (0·18 p.c.), citric (0·65 p.c.), malic (0·30 p.c.), and volatile acids (equivalent to 0·04 p.c. of acetic acid) (Kayser, Zeitsch. öffentl. Chem. 1906, 12, 155). Windisch (Zeitsch. Nahr. Genussm. 1903, 6, 447) and Utz (Chem. Zentr. 1903, ii. 841) have found salicylic acid in pure raspberry juice. The amount obtained was about 1·1 mgrm. per litre of juice, and it is believed to exist as an ester in the fruit. According to Röhrig (Zeitsch. Nahr. Genussm. 1910, 19, 1) formic acid to the extent of 0·000176 p.c. occurs in fresh raspberries. According to Hefelmann, Mauz, and Müller (Zeitsch. öffentl. Chem. 1906, 12, 141), fresh raspberry juice contains on the average 4·09 p.c. of total solids and 0·43 p.c. of ash.

Raspberry juice on keeping becomes cloudy, owing to the formation of ellagic acid, which apparently does not exist as such in the fruit itself, or initially in the fruit juice, but is derived from a tannoid, or from the red colouring matter of the fruit (Kunz-Krause, Arch. Pharm. 1921, 259, 193.

The seeds of raspberries contain 14·6 p.c. of a drying oil of sp. gr. 0·9317, at 15° saponification number 192·3, iodine number 174·8. The liquid fatty acids consist chiefly of linolic and linolenic acids, with small quantities of oleic and *iso*-linolenic acids (Kržižan, Zeitsch. öffentl. Chem. 1907, 13, 263).

Raspberry syrup is made by boiling about 35 parts of raspberry juice with 65 parts of cane sugar. According to Spaeth (Zeitsch. Nahr. Genussm. 1901, 4, 97, 920), in genuine raspberry syrup the amount of ash from 100 grms. should not be below 0·2 grm., and this should require for neutralisation at least 2·0 c.c. of normal acid. The acidity of 100 grms. of the syrup should correspond to from 7 to 13 c.c. normal caustic potash.

A hybrid formed by the crossing of the raspberry with the blackberry has, of late years, come into favour as a fruit. It is known as the loganberry. The plant is a vigorous-growing climber and the fruit is mulberry-shaped and red in colour. The acidity of the fruit is due chiefly to citric acid, though tartaric and volatile acids are also present; malic acid is absent (for analyses *v.* Daughters, J. Ind. Eng. Chem. 1918, 10. 30). H. I.

RASPITE *v.* STOLZITE.

RAURACIENNE *v.* AZO- COLOURING MATTERS.

RAVISON OIL. The oil from Black Sea rape seed, a kind of wild *Brassica campestris*, is termed in commerce Black Sea rape oil or ravison oil. The seed contains 33–40 p.c. of oil.

Ravison oil has a higher iodine value than rape oil, and exhibits stronger drying properties. It is therefore not so suitable for lubricating purposes as the latter, and its admixture with, or substitution for, rape oil must be looked upon as adulteration. Since ravison oil is usually extracted by means of solvents, traces of the latter are left in the oil. They are most readily detected by taking the flash point of the oil. For the characteristics of the oil, *see* tables under OILS, FIXED, AND FATS.

J. L.

REALGAR (*Sandaracha* of the ancients). Native arsenic monosulphide, AsS, crystallising in the monoclinic system. Crystals are not infrequent; these are transparent with a bright aurora-red colour and a brilliant lustre; but on exposure to light they very soon crumble down to a yellow powder consisting of a mixture of arsenic trioxide and arsenic trisulphide. Realgar is found, associated with orpiment (*q.v.*), in mineral-veins at several places in Hungary, and at Allchar in Macedonia; and in beds of sandy clay at Mercur in Utah. It is apparently mined in some quantity in Persia and China. Realgar has been used in calico-printing, in tanning for removing the hair from skins, and in the manufacture of shot. Mixed with saltpetre, it gives the ' white fire ' of pyrotechnic displays. The material now used is prepared artificially from the white arsenic derived from mispickel. The Chinese use fused realgar for coating cups and various ornamental objects. L. J. S.

REAUMUR'S PORCELAIN. Glass in the process of working will often acquire a peculiar opacity. This appears to depend on a physical change, since by a carefully-constructed process a kind of crystallisation may be set up, producing the porcellaneous appearance. Reaumur attempted to introduce a material of this description in the place of pottery (Ure).

RECTIFICATION is the term applied to the second and subsequent distillations of a volatile liquid to free it from the impurities which may have passed over in the first distillation. More particularly applied to the distillation of alcohol (*q.v.*): *v.* also DISTILLATION.

RED, ANISOLE, *v.* AZO- COLOURING MATTERS.

RED ANTIMONY. *Antimony oxysulphide* or *kermesite v.* ANTIMONY.

RED, ARCHIL, *v.* AZO- COLOURING MATTERS.

RED CHALK. An earthy or argillaceous iron ore, used as a drawing or marking material; also in geology for beds of chalk of a brick-red colour (a calcareous rock coloured by ferric oxide) (*v.* REDDLE).

RED, CHROME. *Basic lead chromate v.* CHROMIUM.

RED, CLARET, *v.* AZO- COLOURING MATTERS.

RED CLOVER FLOWERS, *Trifolium pratense* (Linn.), which have a limited application in medicine as an alterative, and in the treatment of cancer, have been examined by Power and Salway (Chem. Soc. Trans. 1910, 97, 231), and found to yield 0·028 p.c. of essential oil, containing furfuraldehyde of sp.gr. 0·9476 at 20°/20°; α_D+4° 0′ in a 1 dcm. tube; a large amount of sugar giving *d*-phenyl glucosazone (m.p. 205°); salicylic and *p*-coumaric acids; *iso*-rhamnetin $C_{16}H_{12}O_7$ (m.p. 295°), probably present as a glucoside; and a number of phenolic substances, among them—*pratol*, a hydroxymethoxy flavone, $C_{15}H_8O_2(OH)(OCH_3)$; *pratensol* $C_{17}H_9O_2(OH)_3$ (m.p. 210°); and the following glucosides: *trifolin* $C_{22}H_{22}O_{11},H_2O$ (m.p. 260°), which yields on hydrolysis *trifolitin* $C_{16}H_{10}O_6$ (m.p. 275°), and rhamnose; *iso-trifolin* $C_{22}H_{22}O_{11}$ (m.p. 250°), and a glucoside of quercetin (m.p. 235°). From the resin in the dried flowers, which was present to the extent of 5·6 p.c., were obtained *myricyl alcohol, heptacosane, hentriacontane; sitosterol;* a dihydric alcohol, *trifolianol* $C_{21}H_{34}O_2(OH)_2$ (m.p. 295°); and a mixture of fatty acids, consisting chiefly of palmitic, stearic, and linolic acids, with small amounts of oleic, linolenic, and *iso*-linolenic acids.

RED, CONGO, *v.* AZO- COLOURING MATTERS.

RED COPPER ORE *v.* CUPRITE.

RED CURRANT, *Ribes rubrum* (Linn.). The fruit is used for table purposes. According to König, the average composition of the ripe fruit is—

Water	Protein	Free acid, malic	Invert sugar	Cane sugar	Other N-free extract	Fibre and seeds	Ash
84·3	0·5	2·2	6·4	0·1	1·2	4·6	0·7

According to Guignard (Compt. rend. 1905, 141, 448), the leaves of red currant contain a substance which yields hydrocyanic acid in small quantities, the largest amount, in June, being about 0·0025 p.c. of hydrogen cyanide; the twigs contain very little and the roots none. For a study of the fermentation of red currant juice and analyses of the resulting wine, *see* Keim (Zeitsch. anal. Chem. 1891, 30, 401).

H. I.

RED, DIAMINE, *v.* AZO- COLOURING MATTERS.

RED DURA. The 'Red Dura' or 'Durra' of the Soudan, also known as 'Shikytan,' consists of the deep reddish-brown sheaths of a grass, apparently the *Andropogon Sorghum* (Brot.) var. *vulgaris*, also known as the *Sorghum vulgare* (Pers.) or 'Great millet,' the grain of which provides so important a foodstuff. According to E. P. Browne, Inspector of the Blue Nile Province, the 'shikytan' is used for producing a red dye, practically utilised for staining a grass called 'lanzura,' employed in the manufacture of coloured 'brush' mats, but occasionally for the leather of 'markubs' (Sudanese shoes). It is specially grown for dyeing purposes. A full account of the *S. vulgare* is given by Watt (Dictionary Economic Products of India, 6, iii. 289). The grain occasionally possesses a brick-red colour, and that at Harihar is used for preparing a red morocco from goat skin. The canes of *S. saccharatum* also, when pressed and allowed to ferment, develop a red or reddish-brown colour, and the dye thus produced can be extracted by means of dilute alkali. The Indian, Persian, Abyssinian, and Egyptian forms would seem to be derived from the *A. Sorghum*, var. *durrha;* but the fact that this plant is so extensively cultivated in Egypt as a foodstuff and the 'Shikytan' is grown entirely for dyeing purposes, seems to indicate that this latter is again a special variety.

The colouring matter, *durasantalin*, to which the formula $C_{16}H_{12}O_5$ has been provisionally assigned (Perkin, Chem. Soc. Trans. 1910, 97, 220), consists of a bright-red or scarlet powder, possessing an ill-defined crystalline structure. It is soluble in alkalis with a red-violet colour, passing rapidly to brown on air oxidation, gives with alcoholic ferric chloride a brown liquid, and when fused with alkali, p-*hydroxybenzoic acid* and *phloroglucinol*, together with a trace of a third substance, probably p-*hydroxyacetophenone*, are produced. Durasantalin does not dye mordanted calico, but behaves as a substantive dyestuff towards wool upon which it produces a dull-red shade. A very permanent and slightly duller colour can be produced by previously mordanting the wool with chromium. In many respects this dye resembles the santalin of sanderswood, but there is no doubt that these substances are chemically distinct.

A. G. P.

RED, FAST, *v.* AZO- COLOURING MATTERS.

RED FIRE *v.* STRONTIUM.

RED HÆMATITE or red iron-ore, *v.* HÆMATITE.

RED, HESSIAN, *v.* AZO- COLOURING MATTERS.

RED LEAD. *Minium* Pb_3O_4 *v.* LEAD.

RED LIQUOR. *Crude aluminium acetate v.* ACETIC ACID; also WOOD, DESTRUCTIVE DISTILLATION OF.

RED MANGANESE. Known also as *dialogite v.* RHODOCHROSITE and RHODONITE.

RED, NAPHTHAMINE, *v.* AZO- COLOURING MATTERS.

RED OCHRE. Oxide of iron mixed with argillaceous matter.

RED OIL *v.* OLEIC ACID.

RED ORPIMENT. *Realgar* (*q.v.*).

RED PRECIPITATE. *Mercuric oxide*, HgO, *v.* MERCURY.

RED SHORT. Iron and other metals which are brittle at a red heat are said to be red short.

RED SILVER ORE *v.* PROUSTITE and PYRARGYRITE; also SILVER.

RED, VENETIAN, *v.* PIGMENTS.

RED WOOD *v.* BRAZILWOOD.

REDDLE or **RUDDLE** is a soft, red, iron ore, more or less impure, commonly associated with deposits of hæmatite, as in the Forest of Dean, at Ulverston, and at Whitehaven. It may be regarded as a kind of red ochre, mixed with argillaceous matter, and is used chiefly for marking sheep.

REDONDA PHOSPHATE *v.* under art. Alums; also Fertilisers and Phosphorus.

REDRUTHITE. A variety of cuprous sulphide, known as *chalcosine*, *copper glance*, or *vitreous copper* found in Cornwall, particularly in the neighbourhood of St. Just, in various parts of Scotland, and both crystallised and massive in the porphyritic district in Ulster, and at the Kenmare mines, Kerry. *V.* Copper glance.

REDUCTASES *v.* Fermentation.

REDUCTION. The abstraction of an electronegative element from, or addition of an electropositive element to, any compound; thus an oxide, deoxidised by the action of hydrogen, charcoal, &c., is said to be reduced. The addition of hydrogen to an organic compound by the action of sodium amalgam, &c., is also called an operation of reduction.

REFRACTOMETER. In the chemical examination of liquids and solutions a knowledge of the refractive index is very often valuable. Such a method of characterisation, however, could not become of any very general practical

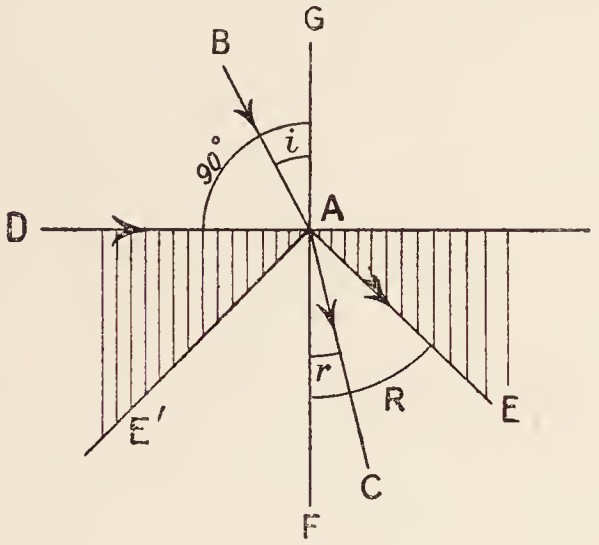


Fig. 1.

utility so long as a spectrometer and a hollow prism were necessary in the determination of refractive power. A rapid and accurate measurement of the refractive index of a liquid with a small quantity of material has become possible only by the introduction of instruments based on the principle of total reflection, and such instruments now play an important part in various branches of analytical practice (J. Soc. Chem. Ind. 1919, 38, 139T).

If A is a point in the common surface of two media, the upper of which is air, and the lower some pure liquid, then the ray of light BA, on entering the denser medium, is refracted nearer the normal GAF in the direction AC, so that $\frac{\sin i}{\sin r}=n$, where n is the refractive index of the liquid. The ray DA, entering the liquid at A under grazing incidence will be refracted according to the same law, and we have accordingly $\frac{\sin 90°}{\sin R}=n$. Obviously, R is a limiting or critical angle, and it is impossible to illumine the shaded part of the denser medium by any rays entering at A; AE is therefore a boundary between light and dark. Conversely, if A is illumined from the side of the denser medium, these rays which proceed from points in the shaded area cannot pass out into the air, but are totally reflected. Further, it is clear from the relationship $\frac{\sin 90°}{\sin R}=n$ that if we can determine the critical angle R, the index of refraction of the lower medium is easily evaluated. Instruments which have for their object the measurement of this critical angle are known as 'refractometers,' and an actual observation with one of these consists in the determination of the position of a boundary between light and dark, such as that referred to above. For a more detailed discussion of the principles underlying refractometry, *see* Philip, J. Soc. Chem. Ind. 1919, 38, 139T).

The instruments chiefly used either for purely scientific or technical chemical work are (1) Pulfrich's refractometer, (2) Abbe's refractometer, (3) the butter refractometer, (4) the dipping refractometer. In connection with the question of the accuracy attainable with such critical angle refractometers, reference should be made to Simeon (Proc. Phys. Soc. London, 1918, 30, 190).

The Pulfrich Refractometer.—The essential part of this instrument is a rectangular glass prism (*see* Fig. 2), so mounted that of the surfaces which are at right angles to each other, one (AB) is horizontal, and the other (CD) is vertical. On the top of the prism there is cemented a small glass vessel, which contains the liquid under investigation. It is essential that the index of refraction of this liquid should be less than that of the prism. The horizontal surface AB is illumined by monochromatic light entering the liquid from the left. If the ray which passes from the liquid into the prism under grazing incidence is considered, its path will be as shown in Fig. 2, and will be marked by a boundary between light and dark. The position of this limiting ray, after it has passed out of the prism into the air, is known when the angle i which it makes with the horizontal is determined. This is effected with the aid of a telescope fitted to a moving circular scale, the

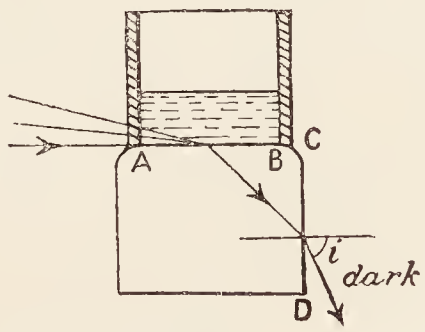


Fig. 2.

crosswires of the telescope being adjusted to the boundary between light and dark.

It can easily be shown that, if n is the index of refraction of the liquid under investigation and N is the index of refraction of the glass prism, $n=\sqrt{N^2-\sin^2 i}$. The value of N having been determined once for all, the index of refraction of the liquid can be easily deduced from the observed value of i. In actual practice tables are supplied with each instrument, in which, for a given prism at a given temperature and for sodium light, the corresponding values of i and n are recorded.

In view of the variation of refractive power with change of temperature, it is essential to

keep both liquid and prism at a definite constant temperature. This is done by passing a current of tempered water through the mount in which the prism is set and also through a silver vessel which is lowered into the glass cell containing the liquid. Reference will be made later to the methods of securing a water current of steady temperature. The adequacy of the temperature control in the Pulfrich refractometer, when used with liquids at temperatures considerably above 20°C., has occasionally been questioned (Lowry, J. Soc. Chem. Ind. 1919, 38, 146T; *cf.* J. Chem. Soc. 1922, 121, 1341).

Fig. 3 shows the general appearance of Pulfrich's refractometer. The mount in which

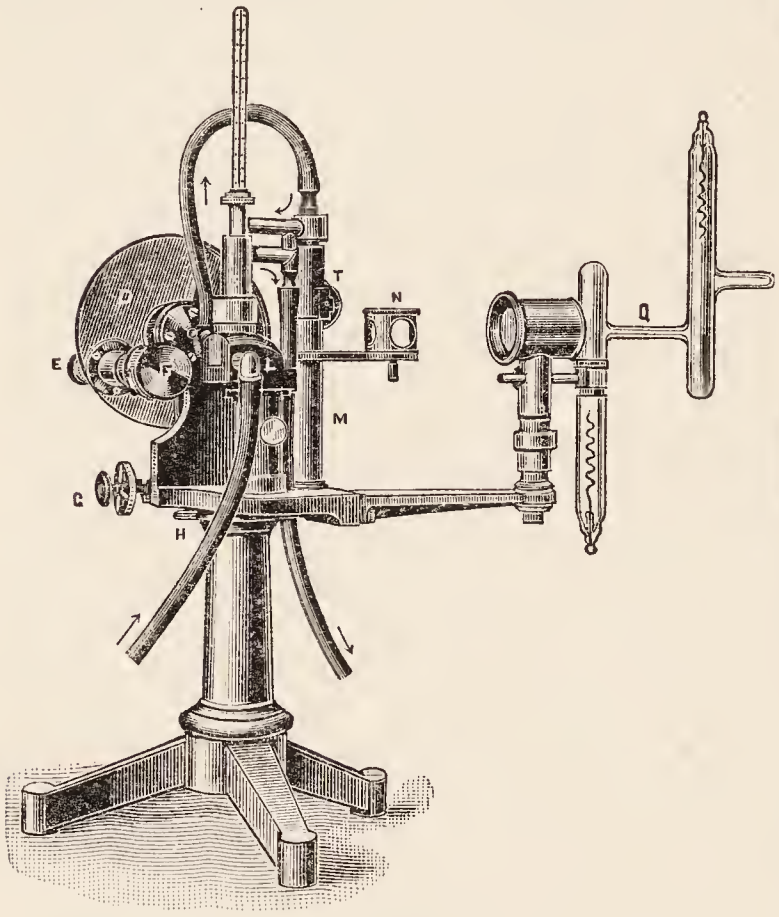


Fig. 3.

the prism is set is seen at L, surmounted by the short glass cylinder which the liquid contains. S, the silver vessel through which the water current circulates, is raised or lowered by means of a screw, and can be moved to one side on the axis M. The telescope EF is fitted rigidly to the divided circle D, which is free to rotate except when clamped by the screw just seen at H. The final adjustment of the cross-wires to the boundary between light and dark is made by means of the micrometer screw G. Connected with this screw there is a graduated drum-head moving in front of a horizontal scale, so that it is possible to determine accurately the dispersion for any given liquid.

As source of light, either a coloured flame or a Geissler tube (as at Q) may be employed. In the former case the burner is set up on one side and the image of the flame is thrown into the liquid by means of the prism N. This prism is movable about M as an axis, and can be displaced when it is desired to use the Geissler tube. The mercury or cadmium lamp also has been suggested as a source of reference lines in refractometric work (*see* Lowry, J. Soc. Chem. Ind. 1919, 38, 147T).

The Pulfrich refractometer, although chiefly used for investigations of a purely scientific nature, has been employed in the estimation of alcohol and extract in beer and wine (*see* Riegler, Zeitsch. anal. Chem. 1896, 35, 27; Race, J. Soc. Chem. Ind. 1908, 27, 544, 547). The accuracy of the instrument is 1 unit in the fourth decimal place in measurements of refraction, and 1–2 units in the fifth place in measurements of dispersion. Although designed mainly for the determination of the refraction and dispersion of liquids, Pulfrich's refractometer can be employed also in the optical investigation of solid bodies. In this case the small glass cylinder is removed, and the polished object is placed on the top of the prism of the apparatus. Contact between the two solids is secured by introducing a drop of a liquid with a refractive index greater than that of the body under investigation. For the majority of glasses monobromonaphthalene is a suitable liquid to use in this way. For observations on the use and design of Pulfrich refractometers with a theoretical investigation of the various errors to which the measurements are liable, *see* J. Guild, Proc. Phys. Soc. London, 1918, 30, 157.

Attention may be drawn to another refractometer (*see* Lewkowitsch, J. Soc. Chem. Ind. 1909, 28, 773) which bears a general resemblance to the Pulfrich instrument, but differs from it in that the rectangular prism of the latter is replaced by a cylinder quadrant. This refractometer can be used in determining the refractive power of solid, liquid, or gaseous substances, and it is claimed that the dividing line between light and dark is more sharply defined than in the Pulfrich instrument.

The Abbe Refractometer.—The essential feature of this apparatus, primarily designed for the investigation of fluids, is a double prism which can be rotated about a horizontal axis. The double prism consists of two similar rectangular prisms of highly refracting glass placed with their hypotenuse faces in contact and mounted in hollow metal cases. The lower prism with its case is removable, but usually hinges at one edge with the other case, and is kept in position by a clamp. When an observation is to be made the double prism is opened out, and a few drops of the liquid under investigation are placed on the ground surface of the lower prism. The prism faces are then brought together, the apparatus being inclined to an angle so that the liquid does not run off, and the clamp is fixed. A thin film of the liquid is thus enclosed between the two prisms. White light is thrown into the lower prism by means of a plane mirror mounted on the base of the instrument, and each point, therefore, on the ground surface of this prism becomes a centre of radiation. Each point, then, on the polished face of the upper prism will be illumined by rays coming from all directions through the liquid. Provided that the index of refraction of the upper prism is greater than that of the liquid, and supposing for the moment that monochromatic light is being employed, the rays converging on any selected point A (*see* Fig. 4) will

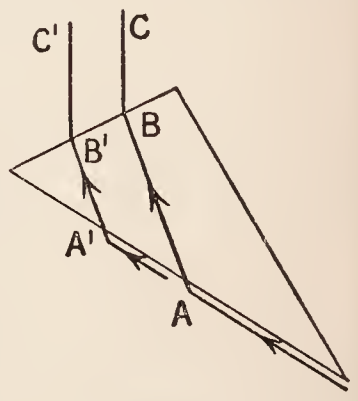


Fig. 4.

all pass into the upper prism, but the one which enters at grazing incidence will give a limiting ray AB in the upper prism, corresponding to a boundary between light and dark, so far as illumination at A alone is considered. Similarly, from any other selected point A′ there will pass through the prism a limiting ray A′B′, parallel to AB. When they emerge from the prism, all these limiting rays will still be parallel, as BC, B′C′, &c.

The telescope of the Abbe refractometer, F in Fig. 5, contains a lens which focusses these parallel limiting rays at the point in the telescope where the crosswires are placed. If it is borne in mind that the prisms have a definite width, it is clear that in the field of the telescope all the limiting rays will be focussed to a line,

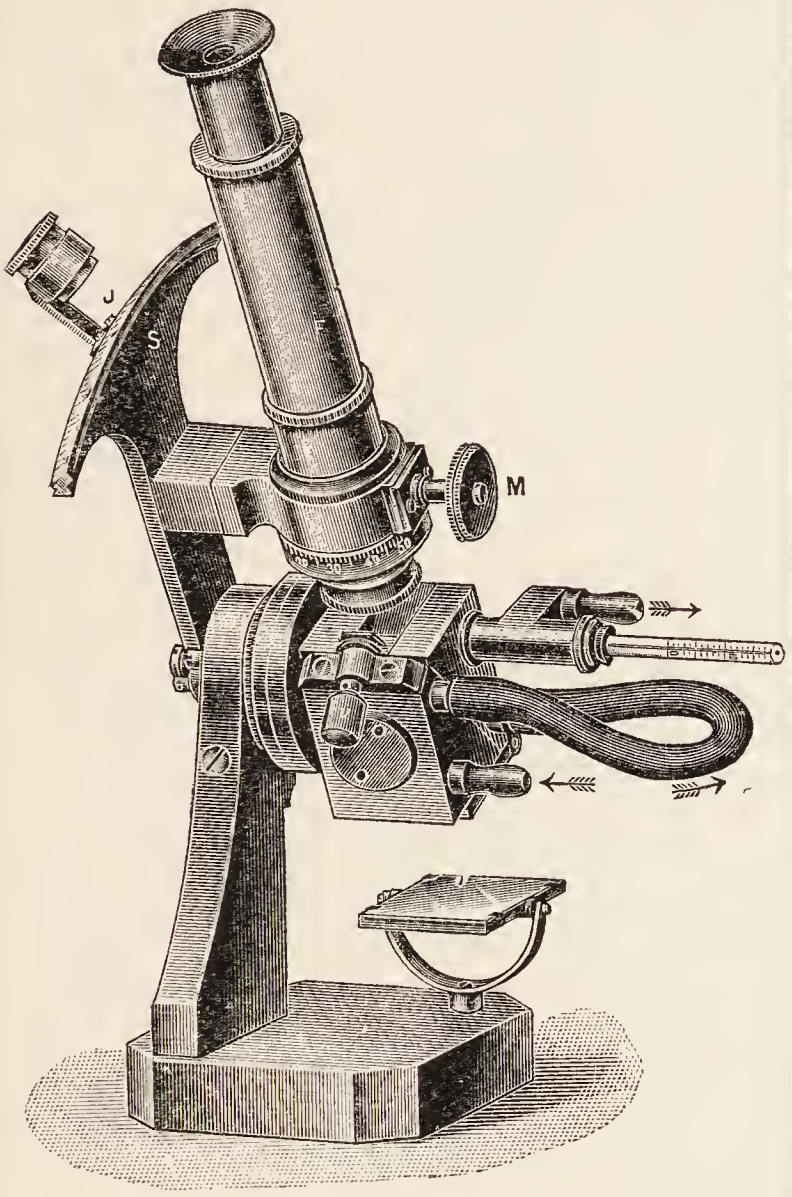


Fig. 5.

which will be a boundary between light and dark. In using the Abbe refractometer the double prism is rotated by the arm J until this boundary passes through the intersection of the crosswires of the telescope. The angle of adjustment of the arm is quantitatively related to the refractive index of the liquid, and might be used to compute the latter. In the Abbe instrument, however, the index of refraction of the liquid is read off directly on a graduated sector, S, which is rigidly connected with the telescope.

When, as is usual, this refractometer is used with ordinary white light, the boundary between the light and dark halves of the field is generally coloured, and no exact adjustment is possible. To obviate this difficulty a compensator is introduced in the telescope between the objective and the double prism. This compensator consists of two Amici prisms which can be simultaneously rotated in opposite directions about the axis of the telescope by means of the screwhead M, and so neutralise the dispersion of the border-line. A reading of the scale of the drum of the compensator permits a computation of the mean dispersion for the liquid under investigation.

The accuracy of the Abbe refractometer is about 2 units in the fourth decimal place of the refractive index. In view of the variation of the refractive power of liquids with temperature, it is essential in accurate work to keep the prisms and the liquid at a definite constant temperature. Provision is made in the Abbe instrument for circulating water of constant temperature through the double-walled metal cases in which the prisms are mounted.

The Abbe refractometer has been employed in the examination of edible fats and oils, lubricants, alkalis, linseed oil, varnish, turpentine, petroleum, paraffin, beeswax, glycerol, aniline, aqueous, alcoholic, and ethereal solutions, milk serum, jams, jellies, and confectionery. So far as the examination of the majority of fats and oils is concerned, the Abbe instrument has to a large extent been displaced by the butter refractometer described below. The range of the former, however, is much wider than that of the butter refractometer, and the Abbe instrument is necessary for use with the highly refracting essential oils. Further, it stands a high temperature better than the butter refractometer, and is therefore particularly well adapted for the examination of substances with a high melting-point, such as beeswax and paraffin.

The Butter Refractometer.—The main parts of this instrument are a telescope and a double prism. As in the Abbe instrument, the two prisms are mounted in metal cases with double walls, in order to permit the circulation of a current of water of constant temperature. The upper prism, however, is rigidly connected with the telescope, while a further difference from the Abbe instrument consists in the absence of a compensator in the telescope. The upper prism is specially constructed so that the border line of total reflection is achromatised for pure butter when white light is used for illumination. The telescope objective is adjustable in a slide by means of a micrometer screw (seen at C in Fig. 6), and in the focal plane of the objective there is placed an arbitrary scale, graduated from −5 to +105, the scope of which covers the interval from $n_D=1{\cdot}42$ to $n_D=1{\cdot}49$. The position of the border line of total reflection can, with the help of the micrometer screw, be determined to within one-tenth of a scale division, corresponding with an accuracy of 1 unit in the fourth decimal place of the refractive index. Each instrument is accompanied by a table, which gives scale divisions in terms of refractive indices, and *vice versâ*.

When a fat or oil other than butter is enclosed between the prisms, the border line of total reflection is more or less coloured. The fringe is blue when the dispersive power is higher, and red when the dispersive power is lower, than that of butter fat. In the examination, therefore, of a sample of butter for adulteration it is desirable to note, not only the exact position of the border line, but also its appear-

ance. The band of colour seen at the border line with fats and oils other than butter fat is in the majority of cases not broad enough to interfere

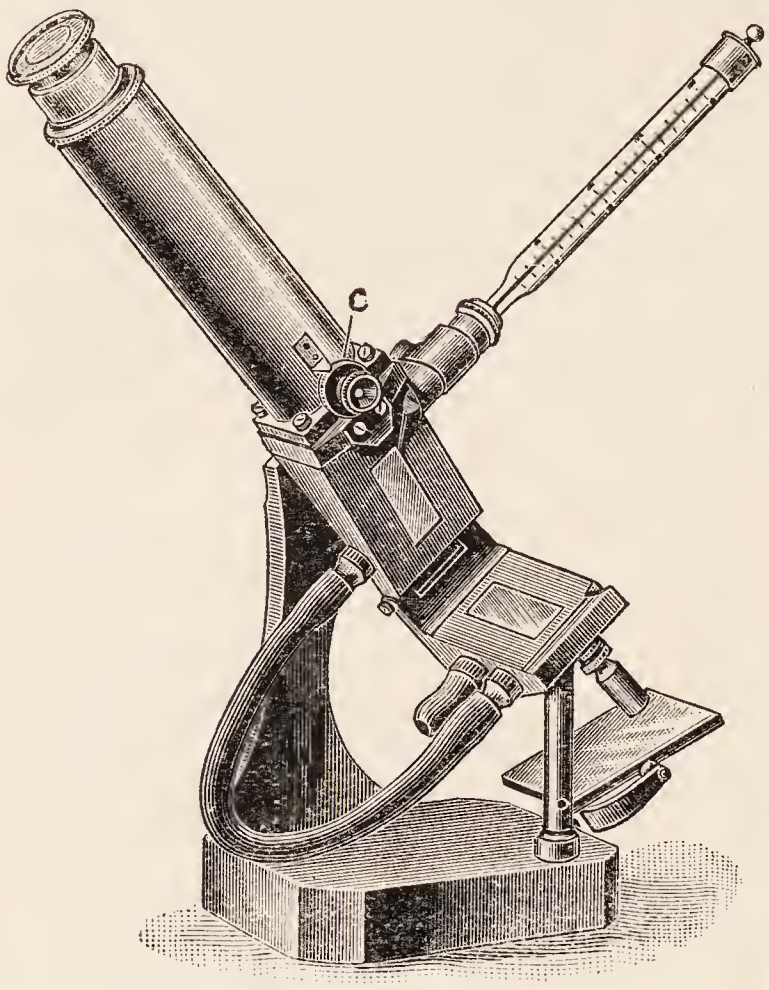


Fig. 6.

with a satisfactory reading. Should an exact reading be impossible, it is advisable to use a sodium flame as the source of illumination.

In the following table there are recorded the scale readings observed for various fats and oils in the butter refractometer at standard temperatures :—

Fats at 40°		Oils at 25°	
Butter . .	40·5–44·4	Cottonseed oil	67·6–69·4
Margarine .	50·3–58·2	Linseed oil .	87·5
Oleomargarine	48·6–49·2	Almond oil .	64·0–64·8
Beef tallow .	49·0	Poppyseed oil	72·0–74·5
Lard . .	50·0–51·2	Olive oil .	62·0–62·8
Goose fat .	50·0–50·5	Colza oil .	68·0
Mutton tallow	45·0–46·0	Sesamé oil .	67·0–69·0
Cocoanut oil .	33·5–35·5	Cod liver oil .	75·0
Cacao butter .	46·0–46·5		

The position of the border line for a given fat or oil varies with temperature, the mean variation amounting to 0·55 scale division per degree centigrade. The scale reading becomes lower as the temperature rises. For the conversion of a reading taken at any temperature into the equivalent value at the standard temperature various rapid methods have been suggested (*see* Leach and Lythgoe, J. Amer. Chem. Soc. 1904, 26, 1193 ; Richmond, Analyst, 1907, 32, 44). In this connection mention may be made also of Wollny's device of using the thermometer itself as an indicator of the highest scale values admissible in the case of pure butter at various temperatures between 30° and 40°. C. H. Wright (J. Soc. Chem. Ind. 1919, 38, 392T) has shown that the modulus of thermal expansion of all oils and fats is the same, viz. 0·000756. Hence it is possible to calculate the refractive index of a fixed oil at any temperature from its refractive index at any other temperature.

Although primarily designed for the examination of butter and allied fats, the butter refractometer has been utilised also in testing such products as varnish, turpentine, petroleum, and glycerol.

Roberts (Analyst, 1916, 376) gives the formula $1{,}000[n]_D = 1{,}422 + 0{\cdot}817x - 0{\cdot}00142x^2$ for the calculation of a refractive index from the scale reading, whilst for calculating a scale reading from a refractive index Liversedge (Analyst, 1919, 49) suggests scale reading $= 287{\cdot}3 - \sqrt{97{,}996 - 703{,}235([n]_D - 1{\cdot}4)}$.

Another instrument which closely resembles the butter refractometer is the milk-fat refractometer. This apparatus is designed for the determination of fat in milk, and the scale covers the interval from $n_D = 1{\cdot}33$ to $n_D = 1{\cdot}42$. The milk is curdled, the fat is extracted with a definite quantity of ether, and the refractive power of the ethereal solution is determined in the refractometer. The construction and manipulation of this instrument are the same as in the case of the butter refractometer.

The Dipping or Immersion Refractometer.—A considerable extension of refractometric methods in chemical work has resulted from the introduction of this instrument. It is especially suited for the examination of dilute aqueous solutions, of which fair quantities (20–30 c.c.) are available. The characteristic part of the dipping refractometer is the prism, which projects from the lower end of the instrument and is immersed directly in the liquid under examination. The body of the prism is cylindrical in shape, and it is so mounted that nothing but glass comes in contact with the liquid. By means of a mirror white light is thrown into the beaker containing the liquid in such a way that the rays enter the prism at grazing incidence, and give rise to a boundary between light and dark in the manner already described. The various parallel limiting rays are focussed by the objective to a line at the position in the telescope where the scale is placed. This border-line would, in ordinary circumstances, be fringed with colour, owing to the difference in dispersion between glass and liquid. The instrument is therefore provided with a compensator, similar to that already described in connection with the Abbe refractometer. This compensator, situated between the prism and the objective, consists of two Amici prisms, which can be rotated about the axis of the telescope by means of a milled ring.

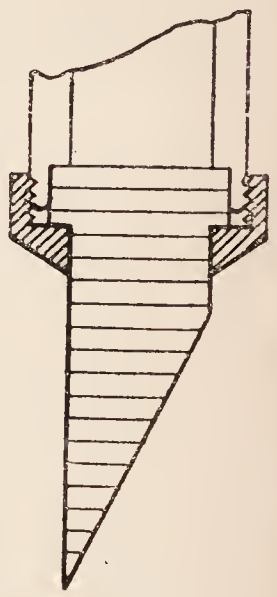


Fig. 7.

The border line is much sharper in the dipping refractometer than in those instruments in which the liquid is enclosed between two prisms. On this ground a higher magnification in the telescope is permissible, and the accuracy of the measurement is correspondingly increased. The scale in the dipping refractometer is graduated from −5 to +105, and covers the range of refractive index from

n_D=1·32539 to n_D=1·36640. With the help of a micrometer screw, which effects the sliding of the scale relatively to the border line, it is possible to ascertain the position of the border line to one-tenth of a scale division, so that the accuracy of the measurement is about four units in the fifth decimal place of the refractive index.

In working with the dipping refractometer a strict control of the temperature is necessary. This is best effected by immersing the beakers which contain the liquids under examination in a bath kept at a constant standard temperature. Care must be taken that the prism of the refractometer and the liquids in the beakers have reached the temperature of the bath before a measurement is made. It is convenient, when large numbers of solutions are to be examined, to have a metal frame in the bath so that the various beakers may be placed in a row and the refractometer slid along from one to another on a wire frame to which it is hooked (Fig. 8).

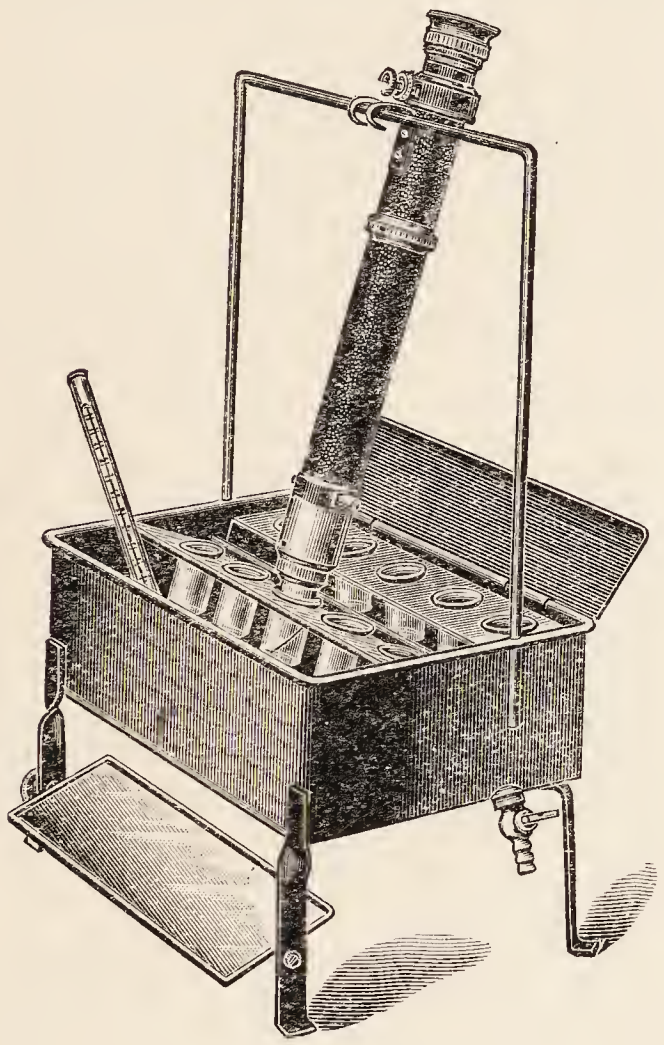


Fig. 8.

If a circular bath is used, the beakers may be arranged in a circular frame, which is moved round so as to bring each beaker in succession under the refractometer. The standard temperature usually employed is 17·5°, at which temperature distilled water gives a scale reading of 15·0.

By various devices the dipping refractometer may be adapted to the examination of certain special cases. A volatile liquid, an ethereal solution for instance, may be enclosed in a metal vessel with a glass bottom ; this fits the end of the refractometer air- and water-tight. The metal vessel is then immersed in the constant temperature bath, and the measurement is made in the usual way. If only a very small quantity of liquid is available, as in the case of blood serum, or if the liquid is deeply coloured, as in the case of dark beers, use may be made of an auxiliary prism. A few drops of the liquid are applied to the hypotenuse face of this prism, which is then slid along the polished elliptical face of the refractometer prism, and is kept in position by the metal vessel already mentioned.

The dipping refractometer has been used in the examination of a large variety of solutions. Provided that there is only one dissolved substance, the refractometer may be employed to determine the strength of the solution, and in this respect it is an instrument of great precision ; it permits, for instance, the detection of as small a quantity of sodium chloride as 2–3 parts per 10,000 of water (Matthes and Wagner, Arch. Pharm. 1903, 241, 241 ; Wagner, Zeitsch. angew. Chem. 1920, 33, 262 ; Clemens, J. Ind. Eng. Chem. 1921, 13, 813). It has been used in the determination of ethyl alcohol in water (Wagner and Schultze, Zeitsch. anal. Chem. 1907, 46, 508 ; Andrews, J. Amer. Chem. Soc. 1908, 30, 353 ; Faust, Zeitsch. anal. Chem. 1919, 58, 145) ; in the detection and estimation of methyl alcohol in aqueous ethyl alcohol (Leach and Lythgoe, *ibid.* 1905, 27, 964) ; in the estimation of dextrose (Wagner and Rinck, Chem. Zeit. 1906, 30, 38) ; in the examination of beer (Ackermann, Zeitsch. ges. Brauw. 1905, 28, 259 ; 1906, 29, 145 ; Barth, *ibid.* 1905, 28, 303 ; Stanek and Miskovsky, *ibid.* 1910, 33, 145 ; Dietsche and Grave, J. Inst. Brew. 1920, 26, 54) ; in the detection of watered milk (Matthes and Müller, Zeitsch. öffentl. Chem. 1903, 9, 173 ; Leach and Lythgoe, J. Amer. Chem. Soc. 1904, 26, 1195 ; Ackermann, Zeitsch. Nahr. Genussm. 1907, 13, 186 ; Mai and Rothenfusser, *ibid.* 1908, 16, 7 ; 1910, 19, 737) ; in the determination of alkaloids (Utz, Chem. Zeit. 1909, 33, 47), and in the medical examination of urine and blood serum (Homer, J. Soc. Chem. Ind. 1919, 38, 145T).

Other refractometers.—In addition to the instruments described above, there are others which have been proposed for use in analytical work. A short reference to these refractometers must suffice.

Amagat and Jean's oleo-refractometer (*see* Muter, Analyst, 1890, 15, 87 ; Richmond, *ibid.* 1892, 17, 321 ; Pearman, *ibid.* 1895, 20, 134) is a differential instrument, the essential parts of which are a collimator, a telescope, and an intermediate metallic vessel, provided with plate-glass sides, and filled with some standard oil. In the middle of this vessel there is a silver receptacle, with glass sides placed at a suitable angle, so as to form a prism. The field is divided into a light and a dark part by means of a shutter, and the position of the edge of this shadow varies with the reference power of the oil which is put in the inner receptacle. The shutter is so adjusted that when the standard oil is put both in the inner and the outer vessels the edge of the shadow is at the zero of the scale in the telescope. When another oil is put in the inner receptacle, the edge of the shadow is displaced to a characteristic position either right or left of the zero.

In Tornöe's apparatus for determining the refraction of beers (*see* Ling and Pope, J. Fed. Inst. Brew. 1901, 7, 170) a modification of Hallwachs' prism is employed, consisting of a rectangular glass trough divided down the middle

by a glass partition, the sides of which are parallel to one another and perpendicular to the end faces. The trough, containing beer in one division and water in the other, is placed on a spectrometer stand, and is illuminated at one end by sodium light. The position of the limiting ray which passes through from the water to the beer is ascertained by a telescope supported on the spectrometer stand and moving round a graduated circle. The trough is then rotated through 180° and the position of the limiting ray, now on the other side of the partition, is determined. From the angle between the two limiting rays the refractive index of the beer can be readily ascertained, and when the refractive index and gravity of the beer are known, the percentages of alcohol and extract can be estimated.

A direct-reading refractometer, suitable for the examination of oils or aqueous solutions, has been designed by Féry (Compt. rend. 1891, 113, 1028 ; 1894, 119, 332). The principle on which the apparatus is based is to annul by means of a solid prism of variable angle the deviation produced in a prism of the liquid under examination. The two prisms are united in one cell, two plano-convex lenses being so cemented together, with the curved faces outwards, that a wedge-shaped space is enclosed. In a form of the apparatus made by Hilger this space is enclosed by two wedge-shaped pieces of glass, and the annulling of the deviation produced in the cell is effected by two plano-convex lenses which form the opposite faces of a surrounding cell filled with water (*see* Fig. 9). The cell fits

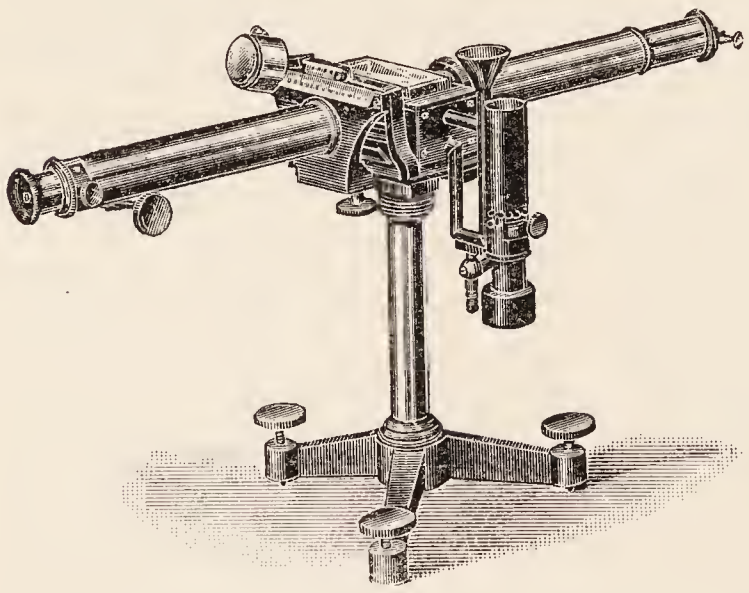


Fig. 9.

in a brass mount with two narrow apertures, 3 mm. high, and one above the other. The lower aperture allows the rays to pass through the base of the cell, which is entirely of glass and acts like a single plane parallel plate ; the upper aperture allows those rays to pass which traverse the liquid. The deviation produced by the liquid in the cell is corrected by moving the cell and its mounting at right angles to the optical axis of the instrument, and from the extent of this lateral movement the index of refraction of the liquid may be deduced. The scale of the instrument, giving the index of refraction directly, extends from $n_D = 1{\cdot}3300$ to $n_D = 1{\cdot}6700$, and the apparatus gives the refractive index with an accuracy of nearly one unit in the fourth decimal place.

For remarks on the accuracy attainable with Critical Angle Refractometers, *see* Simeon, Proc. Phys. Soc. London, 1918, 30, 190.

Supply of water at constant temperature for refractometers.—Reference has already been made to the necessity, in the accurate refractometric investigations of fluids, of keeping the temperature constant. A supply of water at constant temperature may be obtained by running a stream of tap water (the temperature of which is generally constant over a considerable period) at a steady regulated pressure through a heated spiral. Various forms of apparatus have been devised for this purpose (Pulfrich, Zeitsch. Instrumentenkunde, 1898,

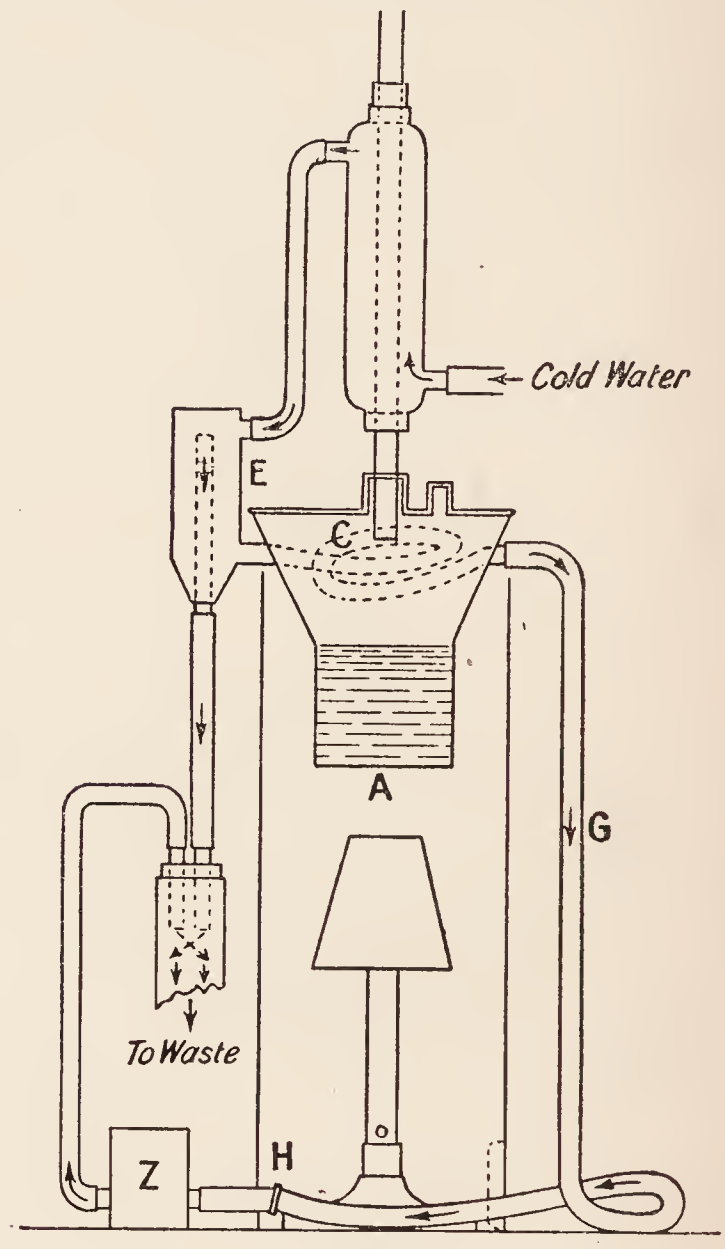


Fig. 10.

18, 49 ; Thorpe, Chem. Soc. Trans. 1904, 85, 257 ; von Heygendorff, Chem. Zeit. 1909, 33, 244 ; Hackman, Chem. News, 1910, 102, 192). The apparatus devised by Thorpe is shown in the adjoining sketch. A is a steam-generating vessel, through the upper part of which there passes the copper or 'compo' tubing C. The stream of water is heated in C, and thereafter passes through the pressure tubing G to the refractometer Z, the rate of flow being regulated by the screw clamp H. E is an arrangement for maintaining a constant head of water at the point of entrance to the coil. The apparatus can be brought into action very quickly, and gives under ordinary conditions a stream of water which does not vary more than 0·1° or so throughout the day.

If a supply of tap water at steady temperature should not be available, it is best to circu-

late water from a constant temperature bath through the refractometer and back to the bath. This is conveniently effected with the help of a small rotary pump, such as that described by Lowry (Trans. Faraday Soc. 1907, 3, 119).

The question of the most appropriate temperature for the recording of refractometric data has been the subject of a report published by the Society of Chemical Industry (J. Soc. Chem. Ind. 1919, 38, 399T). J. C. P.

REFRACTORIES. The term refractories or *refractory materials* has come into general use for *fire-resisting materials*; but the same term is also employed for materials—stoneware, enamels, etc.—intended to resist the corrosive action of liquids, gases, etc., employed in the chemical industries. The manufacture, characteristics, and uses of both types of refractory materials are included among the *ceramic industries*. The manufacture of stoneware and enamels is described in the article on pottery. In what follows, fire-resisting materials are alone considered.

The manufacture of refractory materials is of fundamental importance in the gas, glass, pottery, iron and steel, non-ferrous, and numerous other industries. So important is this that every improvement in the manufacture of refractories has been attended by greater efficiency in other industrial operations. Engineers are waiting for improved refractories, in order to introduce new processes and improve the old ones.

The main refractory materials are (i) fireclay, (ii) siliceous rocks—ganister, quartz, etc., and the like—(iii) magnesite and dolomite. During the War the peak output in refractories per month included 137,465 tons of firebricks, equivalent to nearly 34,250,000 bricks; approximately one-third this number, or 11,159,000 silica bricks; and 684,000 magnesite bricks. Hence, roughly the proportions of firebricks, silica bricks, and magnesite bricks are as 6 : 2 : 1. These products typify what are commonly regarded as the three classes of refractories—neutral, acid, and basic. There are a number of other materials used in smaller quantities—*e.g.* bauxite, zirconia, graphite, chromite, etc.

The distribution of the fireclays and silica refractory materials in Great Britain has been discussed by Mr. Allen Howe in reports from the Geological Survey; there are corresponding reports from many other countries. Reports on the distribution of bauxite and magnesite have been made by the Mineral Resources Bureau, London, and a report on the distribution of graphite by C. Cirkel (1907).

The ultimate composition of fireclays extends over the range indicated in Table I. in next column.

The proportion of silica increases until the siliceous fireclay passes into an argillaceous silica rock and ganister. The last clay indicated in Table I. corresponds very nearly with $Al_2O_3.2SiO_2.2H_2O$, but there are still more aluminous clays. For example, it will be observed that the analysis is expressed in terms of the relative weights of the different components. If the reactions involved in the fluxing of refractories are molecular or atomic, the analysis does not give a direct idea of the relative number of the reacting parts. Thi can be done—

(i) By converting relative weights into relative number of molecular components and reducing the results to the basis-alumina unity.

(ii) By expressing the results in terms of molecular volumes. This would be good if the

Table I.

	1	2	3	4	5	6
SiO_2 .	80·86	72·46	67·46	62·24	54·86	41·44
TiO_2 .	1·00	1 31	1·00	1·00	1·42	1·56
Al_2O_3 .	11·92	17·28	20·45	25·56	29·01	33·71
Fe_2O_3 .	0·81	0·77	2·19	0·94	1·70	1·87
MgO .	0·11	0·36	0·27	0·16	0·40	0·19
CaO .	0·10	0·26	0·18	0·24	0·24	0·44
K_2O .	0·32	1·74	0·90	3·74	0·78	0·40
Na_2O .	0·40	0·48	0·30	0·58	0·48	0·26
Loss on ignition	4·40	5·30	7·40	5·80	10·87	20·60
Ref. test .	29–30	29	29–30	31	32	35

1. Stourbridge siliceous clay (Mobberley and Perry, Stourbridge); 2. Ruabon clay (J. C. Edwards, Ruabon); 3. Leeds clay (Leeds Fireclay Co., Halifax); 4. Devon clay (Jas. W. Gill, Salcombe, S. Devon); 5. Kingswinford clay (J. Walker, Kingswinford); 6. Glasgow clay (Peter and Mark Hurll, Glasgow).

desired information were available. The argument probably is that reactions in refractories can proceed only where the different materials are in contact. The area of the surfaces of contact is dependent on the relative volumes of the components.

(iii) By expressing the composition in terms of (*a*) ideal clay; (*b*) ideal felspar or mica, etc., grouped together as fluxes; and (*c*) quartz. The clay is digested in conc. sulphuric acid and the products soluble in dilute alkali-lye, hydrochloric acid, and water are removed by washing. The soluble portion is considered to be *ideal* clay. The insoluble residue is treated with sulphuric and hydrochloric acids, and the alumina is determined in the residue. The alumina is assumed to come from the fluxes—felspar, mica, etc.—and calculated accordingly. The difference is assumed to be *quartz*. If appreciable quantities of *lime* are present, the lime should be represented separately; similar remarks apply to *ferric oxide*. This procedure is called *rational analysis*. The errors of experiment are so great that a rational analysis estimated from the ultimate analysis is probably more accurate than the observed result.

The action of heat on fireclays in the kilns is somewhat as follows :—

(1) At about 100° the hygroscopic moisture is evolved, and silicic acids and other colloids are to a great extent dehydrated—water-smoking period. These changes are shown by a terrace in the heating curve. A fireclay brick removed from the kiln and cooled shows that it has expanded a little at this temperature. Between 110° and 500° the clay shows a slight contraction.

(2) At about 500° the clay begins to decompose probably into free silica, free alumina, and water. Further, the clay begins to lose its combined water. These changes are shown

by a terrace in the heating curve. The drastic nature of these changes is evidenced by the clay occupying rather a larger volume than before it entered the kiln. The oxidation of any organic matter in the clay now proceeds at a slow rate; as the temperature rises the oxidation occurs at faster and faster rates.

(3) At about 800° alumina in the clay begins to alter its character, and silica begins to change very slowly into tridymite or cristobalite. This change is shown by a hump in the heating curve. The vitrification of some fireclays commences below 1100° although the clay may soften and lose its shape at much higher temperatures, say 1500° upwards; other clays do not begin to vitrify until a much higher temperature is attained.

(4) At about 1100° the free alumina and silica begin to recombine to form *sillimanite* $Al_2O_3 \cdot SiO_2$, which shows itself under the microscope in needle-like crystals.

(5) At about 1500° fireclays usually begin to vitrify to form a hard fritted mass.

(6) At about 1650° the clay may be soft and lose its shape under its own weight.

(7) At about 1700° the clay forms a brown viscid liquid.

These changes are illustrated graphically in Fig. 1.

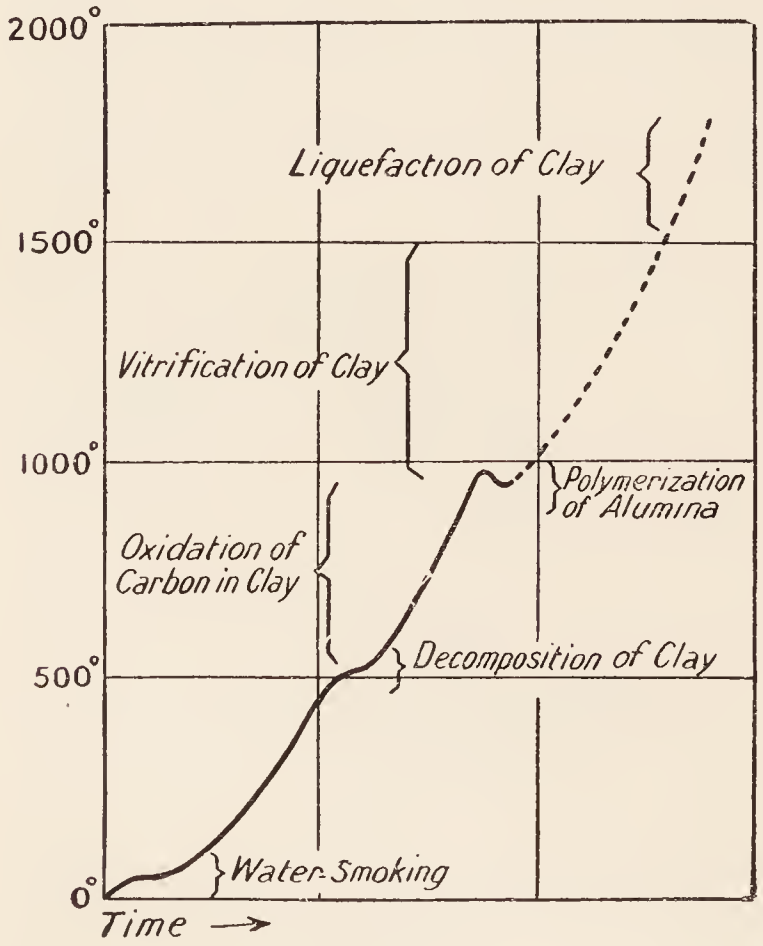


FIG. 1.

A refractory must withstand without deformation the temperature to which it is to be subjected. The fusion test is of prime importance, because a given material is useless as a refractory if it squats below the highest temperature attained in the furnace where it is to be used. There are, however, other important qualities. Resistance to high temperatures under load; resistance to the cutting action of flames under forced draught; reducing atmosphere, the corrosive effects of ashes, flue-dust, slags, salt vapours, etc.; splitting and spalling with rapid fluctuations of temperature, etc. Refractory materials do not have a sharp melting-point; rather do they behave like highly viscous fluids which become less and less viscous as the temperature rises. The so-called squatting or softening temperature is therefore more or less arbitrarily defined at the temperature at which the material begins to lose its shape when heated. The usual signs of this change are the rounding of the sharp edges of the test-piece. Time is an important factor, because the result is determined by the time and temperature. The size of the test-piece, the nature of the atmosphere, and currents of gas in the furnace usually affect the result. When a raw material is being tested it is moulded in the form of a cone, and dried; when a burned product is being tested a portion is chipped and ground into the approximate size of a cone. The test-piece is cemented in the centre of a refractory disc, and surrounded with Seger cones of varying denominations cemented in position by means of a mixture of china-clay and alumina. The temperature of the test-piece and cones is then gradually raised. When the test-piece shows signs of fusion the disc is removed from the furnace, and the refractoriness of the material is estimated to be equal to that of the cone of highest denominations which has squatted. It is assumed that the range of cones employed includes some which have not squatted at all. If all the cones have squatted, the test must be repeated with a set of cones of higher denomination; and if none of the cones have squatted, the test is repeated with cones of lower denomination.

The higher the load borne by the refractory material, the lower the deformation temperature. Tests have therefore been devised to show the softening temperature while the test-piece is subjected to a known pressure—say 50 lbs. per sq. in. The results are remarkable. As a rule there is a relatively large difference in the squatting temperature of the less siliceous, or more aluminous fireclays, than in the case of more siliceous materials. For example, china-clay, one of the most aluminous clays, squatted at cone 35 without load and at cone 19 with a load of 50 lbs. per sq. in., while a siliceous fireclay squatting at 34 without load broke down at cone 26 under a similar load. The relation between the load and the squatting temperature can be represented by the equation

$$\text{squatting temperature} = Ce^{-kw}$$

where C denotes the squatting temperature in cones without load; w denotes the load in lbs. per sq. in.; and k is a numerical constant characteristic of a particular clay, the mode of manufacture, grain-size, etc. In the clays which have been tried k ranges from 0·0111 to 0·0030.

There is no clear relation between the composition and refractoriness of a clay; some clays with 3 p.c. of ferric oxide behave better than other clays with 1 p.c. of that oxide: similarly, some clays with 1·5 p.c. of alkalis give better results than other clays with 0·75 p.c. of alkalis. Generally, however, high proportions of iron, alkalis, or alkaline earths are attended by a low refractoriness. Several empirical formulæ have been proposed to show the relation between composition and refractoriness, but none has proved entirely satis-

factory. The analysis of a clay or firebrick can be reduced to a molar formula, alumina unity. The sum of the molar proportions of the titanic oxide, ferric oxide, magnesia, and the oxides of the alkalis and alkaline earths are regarded as fluxes. The composition of the refractory can be then represented by two variables, x and y, such that

$$x \text{ fluxes} : Al_2O_3 : y\ SiO_2$$

The position of a given refractory on the chart shows the probable softening temperature of the clay in terms of Seger cones. Thus, the first clay indicated in Table I., is represented by the point 6 in the diagram; and according to the rule, it should squat near cone 35; which indeed it does. Of two hundred to three hundred fireclays examined, with a refractoriness exceeding cone 29, about two deviated appreciably from the rule. It does not work well with clays with high proportions of silica. For the purer types of clay involving only three constituents—ideal clay, felspar, and quartz—the fusion curves for all possible combinations are indicated in Fig. 2.

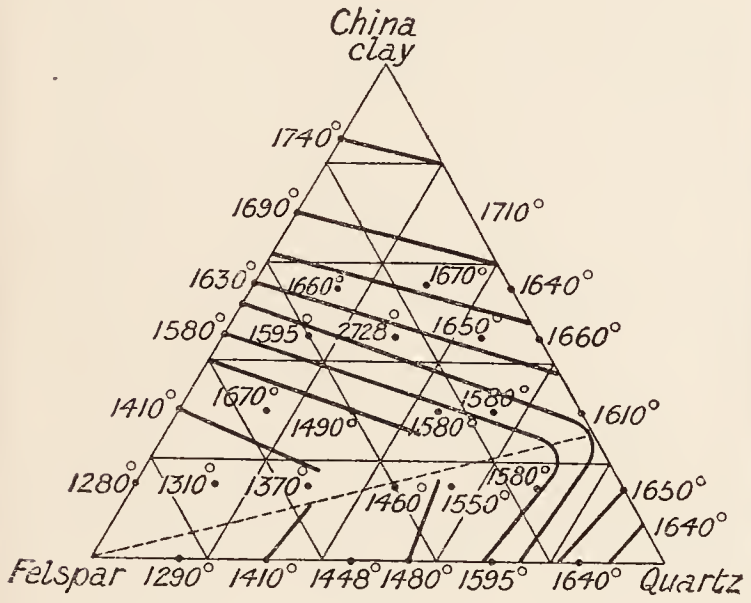


FIG. 2.

The rules take no cognisance of the grain-size, other things being equal; if two materials with the same composition have a marked difference in texture, that with the finer grain-size will squat before the coarser-grained one. The finer the grain the lower the squatting temperature.

Since the reactions between the particles in the firing take place at the surfaces of contact, the speed of vitrification depends on the number of surfaces of contact. For a group of spheres, the number of points of contact varies inversely as the cube of their radius. Hence, reducing the radius of the grains from 1 to 0·0001 mm. raises the number of points of contact from, say, 2160 to 2,160,000,000,000,000.

On the principle that like resists like, acid refractories resist acidic fluxes and basic refractories resist basic fluxes; but basic bricks are rapidly corroded by acidic fluxes, and basic fluxes rapidly corrode acidic bricks. Assuming a refractory of the right composition has been selected, the subsequent behaviour is largely determined by the texture. The texture of a brick may vary from that of the light porous bricks used for heat insulation to the non-porous vitreous bricks used for acid-towers, etc. Close-textured bricks resist fluxes better than those with an open texture.

Slight imperfections in the exposed face of the brick are weak spots which are developed by the slag into salients; the salients are widened and deepened; patches are isolated and imprisoned in the slag. In this particular case, the flank attacks by the slag are most serious. The joints separating the bricks from one another are the weakest places. Here the slag may cut its way until the brick itself is undermined and isolated. Ultimately the brick leaves the setting, rises, and floats on the surface of the slag. Naturally, the use of large bricks would lessen the number of joints, but if the slabs be too large they are particularly liable to crack, and a crack may cause more damage than quite a number of joints. Similar remarks apply to the corrosive action of ashes and flue-dust. Composition and texture are of vital importance.

There is the paradoxical fact that some refractories are doing well in furnaces at a higher temperature than the squatting temperature of the materials. This phenomenon can occur when the intense heat penetrates only a short distance into the substance of the firebrick. The net result is that the bricks behave as if they were faced with a highly viscous varnish. If the fused face be not viscid enough to remain *in situ*, it will trickle down and expose a fresh surface to attack. The brick will then have a short life. Similarly, if the surface skin is liable to spall or split off from the face of the brick, the life will be correspondingly abbreviated. Likewise, too, in resisting fluxes, slags, flue-dust, and salt vapours, if a surface skin is formed which persists *in situ*, a brick chemically unsuitable for resisting a flux may give better results than one whose chemical composition is satisfactory but whose physical properties favour rapid attack. Indeed, in some cases, the workmen smear the face of the bricks with a fluxing agent before introducing the main charge. Hence, not only is the composition, refractoriness, and texture of firebricks to be considered, but the nature of the surface skin formed on the exposed faces of the bricks often plays a vital part in prolonging the life of a furnace.

It is highly important to have the joints as small as possible; to ensure this, the bricks should be of uniform size. Many furnace builders do not appreciate the importance of this point, and they use the bonding cement as lavishly as if it were mortar being used in the building of houses. When such furnaces are down for repairs, it is not uncommon to find the bonding cement has fused and run away from the joints. The bonding cement is usually of a lower refractoriness than that of the bricks, and it should be used as sparingly as possible.

Ordinary firebricks are usually made from a mixture of clay or clays with *grog*—the *chamotte* of the French, and the *Schamotte* of the Germans. The term grog is applied to previously burned fireclay which has been crushed to particles suitable for admixture with the clay. Broken firebricks from dismantled furnaces, when freed from slag, make excellent grog. The texture of firebricks is

largely controlled by the grog. There are a few important points about this material. Grog should be well fired so that it suffers little change when subsequently heated with the clay; grog should be graded in sizes to suit the desired texture. For coarse-grained bricks, most of the dust should be removed. The grains of grog should be angular, so as to ensure better contact and packing. The clay and grog should be thoroughly mixed. Merely pugging the two is usually inadequate; and if the clay and grog are ground together on pans, care must be taken that the grading of the grog is not rendered abortive by the subsequent grinding in the pan. It is usually desirable thoroughly to soak the grog in water before it is mixed with the clay. This ensures a better amalgamation of the grog and clay than if dry grog is added to the wet clay.

Grog serves many other useful functions in clay-working, *e.g.* it enables the drying contraction to be controlled. Clays with a high shrinkage on drying are liable to crack and warp. This tendency is inhibited by the addition of grog. Fine-grained and vitreous refractories have a high crushing strength, but exhibit a great tendency to crack or spall with abrupt changes of temperature. This is regulated by increasing the size and proportion of grog, but the change is at the expense of the crushing and tensile strength of the materials. Increasing the proportion of grog also decreases the plasticity or the working qualities of the clay. The proportion of grog is dependent on the plasticity of clay. Usually 2 : 3 or 3 : 2 are the proportions used. An average grading is 4 p.c. remains on a 4's lawn; 55 p.c. remains on an 8's lawn and passes a 4's lawn; 40 p.c.

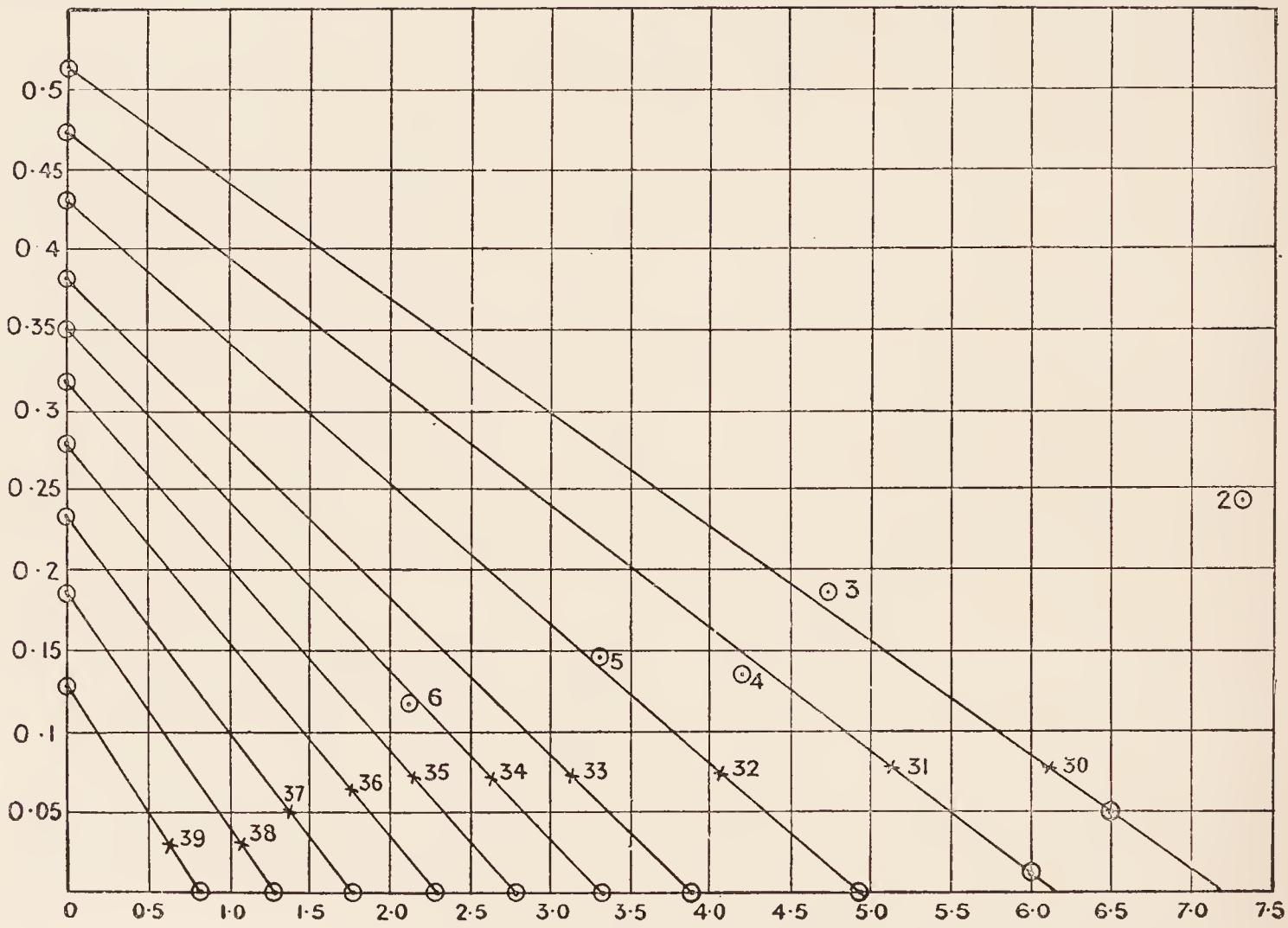


FIG. 3.

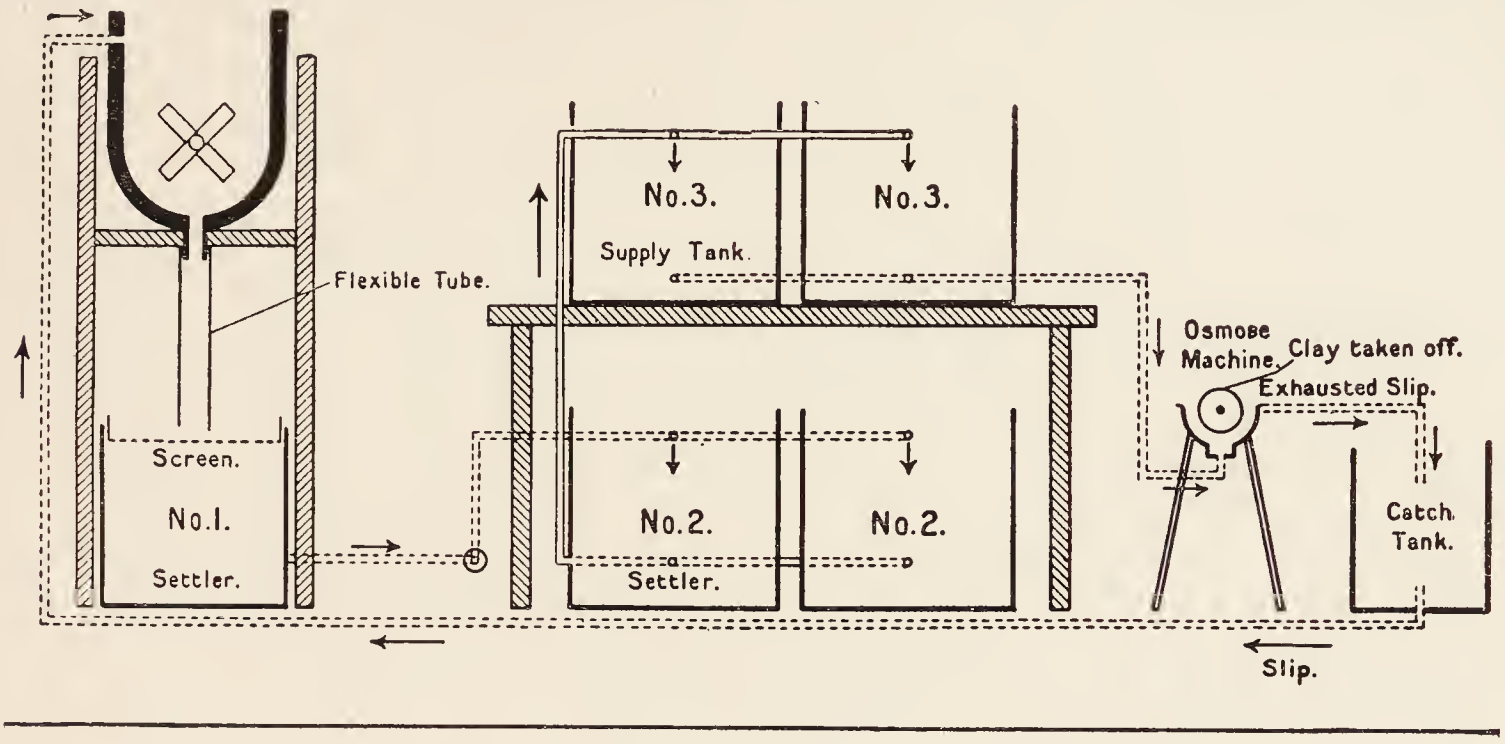
passes an 8's lawn and remains on a 40's lawn; and about 1 p.c. passes a 40's lawn. Antagonistic qualities are involved, one quality can usually be accentuated only at the expense of another. It is again important that the grog be well-burned, and uniformly mixed with the clay.

One great fault in manufacture is inadequate mixing. It is very difficult thoroughly to mix solid materials. In illustration, four hours' churning of a mixture of clays in a power-driven dough mixer does not give a satisfactory result for some purposes. It is not, therefore, reasonable to expect the passage of a mixture of clay and grog, or of a mixture of two or more clays, through many types of pug-mills will do much more than bring the materials together; it will not give an intimate admixture. If a refractory is compounded of a number of constituents inadequately mixed, there will be numerous places in the brick which will have different properties, and spalling, cracking, local fusion or corrosion, etc., may very properly lead to the bricks being condemned.

Some fireclays contain pyrites, and nodules of siderite, as impurities. These are not necessarily shown in the analysis. If the total iron so introduced were uniformly diffused through the clay, it would probably do little harm; but when iron is concentrated in local patches, serious harm may result by the production of a slag, particularly if the refractory be used in a reducing atmosphere. When fireclays containing these nodules are weathered, the clay usually crumbles and the nodules are removed from the exposed face by hand-picking. This is fairly effective in practice although it does not remove the smaller nodules. The purification of fireclays from sand, etc., can be effected by washing. This is a rather expensive process. The clay to be washed is blunged into a *slip* or

thin slurry, mixed with a small proportion of equal parts of soda-ash and water-glass, say 0·3 p.c. The clay remains in suspension, and most of the impurities collect as a sediment. The next problem is to remove the water from the clay. This can be done by the old-fashioned slip-kiln, or by the processes employed in the extraction of china clay in Cornwall, by the filter-press; by Gee's centrifuge; by electro-deposition on a rotary anode as in the so-called Osmose process; by the de-waterer; etc.

Fig. 4 illustrates diagrammatically the continuous process of electric purification. The clay is blunged in the apparatus on the left of



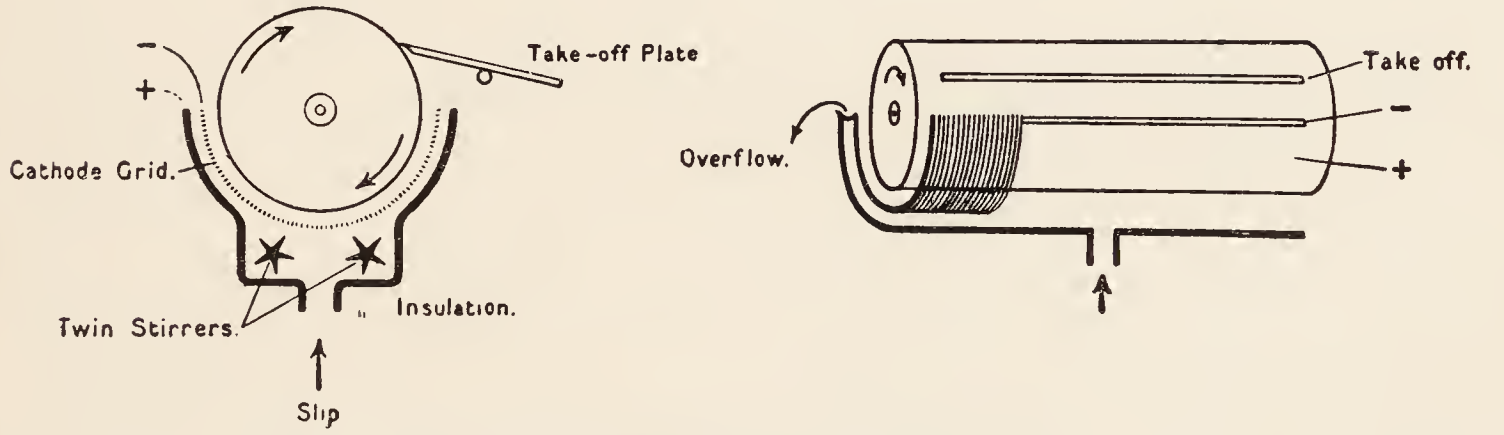


FIG. 4.—Osmose plant (Diagrammatic).

Fig. 4. The slip passes through a screen into No. 1 settler. Sedimentation occurs in tank No. 2; the slip is pumped into tank No. 3. The slip then passes by gravitation through the electrolytic cell with a rotary anode. The water passes back to the blunger. The clay is scraped from the anode as it rotates past the scraper.

The refractoriness of some clays is greatly augmented by washing—in some cases the squatting temperature is raised from cone 28 to cone 35. So, too, the plasticity of the clay is frequently raised by the washing. Whether or not a clay can bear the cost of washing is largely decided by the enhanced value of the improved qualities.

The refractoriness of fireclays can often be improved by intimately mixing them with bauxite or alumina. In some cases, too, crushed quartz or quartzite is added with the grog. The quartzite may fuse at cone 35, but if finely-divided quartz or quartzose sand be intimately mixed with the clay, the refractoriness may be diminished. This has been emphasised by H. Seger and others. The observations of L. Bradshaw and W. Emery are summarised by the graph, Fig. 5.

The quartzose grog should be in coarse

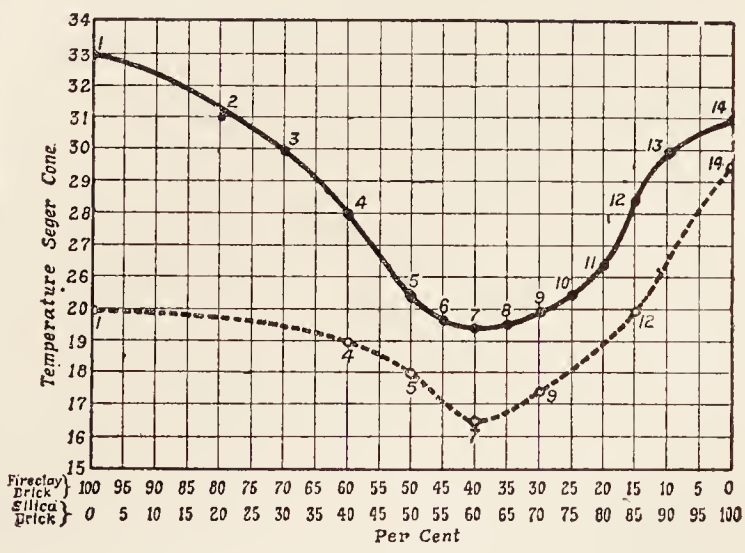


FIG. 5.

irregular-shaped granules; rounded grains do not felt or pack with the clay so well as irregular-shaped grains.

In manufacturing refractory goods, the fireclays are mined and more or less weathered. Care is usually taken in mining to keep definite seams separate. The right proportion and grain-size of soaked grog is added. Other clays may be also introduced, since the working qualities of some clays are improved by blending with other clays. The right proportion of water is added and all thoroughly mixed to form a plastic mass. The clay is then moulded to the desired shape and dried. The dried goods are set in kilns and are supposed to be fired to approximately cone 10–14. The process so outlined is modified to suit local conditions and particular clays.

Some refractories are shaped by dexterously throwing a suitable piece of clay into the mould, and the excess of clay cut off; some are automatically moulded by machinery; and some are made by casting the shrinkage, and then measuring the change in size. A few years ago a 2 to 3 p.c. after-contraction (linear) was common; to-day the average is nearer ½ p.c. Unlike clay, quartz expands on firing, and if quartzose grog is used it is possible to get the expansion of the quartz and the contraction of the clay so balanced that the bricks may be under-fired and yet show virtually no after-contraction when tested under certain definite conditions. It is, however, questionable if this way of evading the after-contraction test with under-fired bricks is satisfactory. With adequate firing, however, the addition of quartz improves firebricks.

Very good results have been obtained by fortifying the clay with carborundum; the fire-resisting qualities have been augmented in a remarkable way. The excellent results obtained are well worth the additional cost. On the other hand, there are failures where the refractory has expanded and disintegrated with these same mixtures similarly treated. So far as one can see the conflict of testimony is extraordinary. The carborundum mixtures have not been in use long enough to bring out the cause of the failure.

The so-called *silica bricks* are made from quartzose rocks; and they have received special names from the parent rocks. Thus, *ganister bricks* are made from the ganister rocks in the neighbourhood of Sheffield; and *Dinas bricks* are made from the quartzite rocks in the Vale of Neath (Glamorganshire). Many attempts have been made to show that ganisters and quartzose rocks should have a specific structure in order to furnish satisfactory silica bricks. The arguments have generally been based on observations made with the raw materials used by particular firms making first-class goods. Other types of raw material have been condemned, but on trial it has often been found that the condemned raw materials have likewise furnished first-class bricks. The only inference to be drawn is that each type of raw material requires specific treatment—otherwise expressed, humouring—to get the best out of it. This remark applies not only to raw silica materials, but also to fireclays.

The changes which occur when quartz is heated are indicated in the article on that mineral. The complex transformations which quartz undergoes are summarised in Fig. 6. It is not possible to translate these hypotheses and facts into works' practice. It suffices to abbreviate the facts and show that quartz has a sp.gr. about 2·65, and when heated it slowly changes into a form or forms with a sp.gr. approximating 2·32. This corresponds with an expansion of about 14 p.c. The expansion plays an important rôle in the behaviour of the bricks. During firing, for example, the bricks expand; and if the transformation be not completed in the burning of the bricks, an expansion occurs when they are in use. The speed of the transformation is dependent on the temperature, the higher the temperature the faster the change. With flints the change is relatively quick, with Sheffield ganister the change is slower, and slower still with Anglesea quartz. The presence of certain mineralisers may also accelerate the conversion from the high to the low sp.gr. form. It is not to be supposed that a complete conversion is desirable, although it has not yet been shown what percentage conversion is desirable with silica bricks for different purposes. In general, it is desirable in burning silica bricks, to convert the

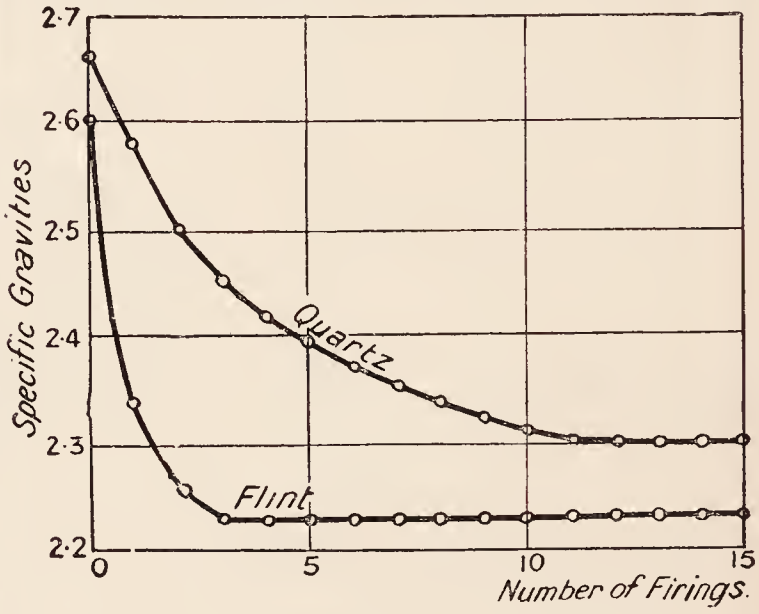


Fig. 6.—Action of heat on quartz.

largest proportion of the quartz into the low sp.gr. form. If otherwise, the permanent expansion of the bricks may produce great strains in the masonry; again, the expansion on the hot face of the brick may produce a local expansion which results in spalling. For the roofs of steel furnaces and certain flues, a slight expansion of the bricks in use makes it desirable to maintain tight joints. Silica slowly volatilises at high temperatures, say 1700°, particularly in contact with carbon.

The plasticity and binding strength of the materials used for making silica bricks is small; and insufficient to enable the moulded bricks to retain this form when dried or fired. Some quartzose rocks and ganister contain sufficient clay to serve as a binding agent. Others require the addition of clay—say 5–10 p.c.—or milk of lime—say 1·5–2·5 p.c. Many other binding agents have been suggested. The quartzose rock is crushed and ground. A kind of average grading is—

Below 120's	80's–120's	40's–80's	4's–40's	on 4's
18	18	20	40	4

Usually, however, no screening or grading is used; it is assumed that experience has taught

the manufacturer that grinding for a particular time in a particular pan will give the best possible result. The mixture is then tempered with the requisite proportion of water or milk of lime by working, say, enough for 250 bricks in an edge-runner pan, until a uniform mixture is obtained—15–20 minutes. The bricks are usually moulded by hand. There is a similar prejudice against machine-made silica bricks as with fireclay bricks. This is largely based on the use of unsuitable machines, or inadequate preparation of the mixture to be moulded. As in the case of firebricks, silica bricks may show laminations which subsequently give rise to spalling. The moulded bricks are dried, set in the kilns, and burned as in the case of firebricks. The earlier stages of the firing of silica bricks is simpler than with fireclay bricks, but the former usually require a much higher temperature than the latter. The cooling of a silica brick kiln also requires some attention, owing to the abrupt change in the coefficient of thermal expansion at about 700°, &c.

Under the microscope, lime-bonded silica bricks are seen to be composed of grains of unconverted or partially converted quartz, with grains of tridymite and cristobalite representing the converted quartz, all embedded in a glassy matrix which may or may not show needle-like crystals of wollastonite. The matrix is a calcium silicate or calcium alumino-silicate glass. According to A. Scott, the distribution of the different forms of silica in a used brick from the roof of a steel furnace is as follows :—

The grey zone which is in contact with the gases consists of a homogeneous aggregate of minute rounded crystals of cristobalite, with sometimes smaller grains of tridymite, the silica occurring in the meshes of a black network, which is composed of magnetite. The original structure of the brick is entirely lost. The black area, which is farther removed from contact with the gases, is composed largely of well-formed wedge-shaped tridymite, with abundant interstitial magnetite. The original rock fragments can be traced while the major portion of the magnetite is found in the matrix. The pale-coloured part, which adjoins the black, shows the same structure as the original brick, but the matrix here contains both high temperature forms while the rock fragments only show partial conversion of the quartz to cristobalite. The reddish part which has been the coolest part of the brick resembles unused material, and contains abundant unaltered quartz in the rock fragments the matrix having much cristobalite. The following table shows how the percentage (by volume) of unaltered quartz varies with the distance from the hot end of the brick :—

Distance from hot end in cm.	19·0	17·0	15·3	13·5	11·2	9·5	8·5	7·5
Percentage of unaltered quartz	53·8	52·0	44·8	40·1	30·7	16·0	3·8	0·0

The refractoriness of silica bricks is usually greater than that of fireclay bricks, and, as previously stated, they do not squat so readily under load. Silica bricks usually disintegrate and become more friable with abrupt alterations of temperature.

As in the case of fireclay bricks, fine-grained bricks resist abrasion and erosion, and possess a greater mechanical strength than coarse-grained bricks; the coarse-grained bricks usually resist abrupt changes of temperature better than fine-grained bricks. The conversion from the high to the low sp.gr. form of silica usually proceeds faster than with coarser-grained bricks. This may be largely due to the accelerating influence of the binding flux.

Table I.—Some General Properties of Refractories.

Material	Refractoriness	Ret. U-load, 50 lb. per sq. in.	True specific gravity	App. specific gravity	P.c. porosity	Coef. thermal expansion, 0°–1000°C.
Silica brick	Conc. 32–35	Conc. 18–30	2·3–2·5	1·7–1·9	20–30	90×10^{-7}
Semi-silica brick	,, 30–32	,, 17–26	2·5–2·6	1·8–2·0	22–30	60×10^{-7}
Firebrick	,, 30–35	,, 14–20	2·5–2·6	1·9–2·1	20–30	40×10^{-7}
Bauxite brick	,, 36–39	,, 14	3·1–3·4	1·8–2·1	30–40	65×10^{-7}
Magnesite brick	,, 39–40	,, 16	3·1–3·5	2·4–2·7	20–30	100×10^{-7}
Chromite brick	,, 40–42	,, 15	3·1–3·6	2·3–2·6	20–30	90×10^{-7}
Zirconia brick	,, 39–42	,, 19	4·8–5·9	4·0–4·6	15–30	$8·4\times10^{-7}$
Carbon brick	,, 39–40	,, 27	2·7–3·1	1·9–2·0	25–30	—
Carborundum brick	,, 42	—	—	—	—	—

Silica refractories with 80–95 p.c. silica are doing useful work as gas retorts, coke-oven bricks, etc. They are not suited for resisting attack by basic slags—*e.g.* alkali, lime, lead, or copper slags; basic flue dusts from producer ash, &c.

During the firing of silica goods the *equilibrium form* of the silica material in the kiln is the 'low specific gravity' form—tridymite or cristobalite. If in the manufacture the conversion to this form is not complete, then, when the silica material is in use, the unconverted silica will slowly pass into the equilibrium form. We have a similar phenomenon with fireclays, the equilibrium form is sillimanite—aluminium silicate Al_2SiO_5. The alumina in fireclays slowly reacts with the silica, and is thereby converted into sillimanite while the bricks are being fired, and when they are in use. Under certain conditions the formation of the sillimanite crystals makes the refractories more brittle; under other conditions—say during the first burning of the bricks—the development of the sillimanite makes the bricks tougher. It has been further shown that the sillimanite form is more chemically inert than other forms. It is therefore desirable as far as practicable to develop this constituent in the bricks during

TABLE II.—MEAN SPECIFIC HEATS OF REFRACTORY MATERIALS BETWEEN DIFFERENT TEMPERATURES.

Material	Composition (main constituents)	Mean specific heat between 25°C. and								
		100°C.	200°C.	400°C.	600°C.	800°C.	1000°C.	1200°C.	1400°C.	Investigators.
Fireclay material	59·2 p.c. SiO_2; 35·3 p.c. Al_2O_3	—	—	—	0·228	—	0·265	0·284	0·297	Bradshaw and Emery
,,	62·23 p.c. SiO_2; 30·42 p.c. Al_2O_3	—	—	0·222	—	0·248	—	0·263	—	Heyn, Bauer and Wetzel
,,	Stourbridge firebrick	0·194	—	—	0·234	0·258	0·261	0·264	—	Holdcroft and Mellor
,,	60·8 p.c. SiO_2; 33·9 p.c. Al_2O_3	0·188	0·197	0·226	0·253	0·249	—	—	—	Y. Tadokoro
,,	—		0·209	0·228	—	—	—	—	—	Steger
Silica material	96·6 p.c. SiO_2; 1·02 p.c. CaO	—	—	—	0·226	—	—	0·282	0·293	Bradshaw and Emery
,,	96·92 p.c. SiO_2; 0·97 p.c. CaO	—	—	0·238	—	0·260	—	0·267	—	Heyn, Bauer and Wetzel
,,	—	—	0·207	—	—	—	—	—	—	Steger
,,	95·0 p.c. SiO_2; 3·06 p.c. CaO	0·186	0·199	0·240	—	0·250	—	0·247	—	Y. Tadokoro
Magnesite material	53·3 p.c. MgO; 22·5 p.c. SiO_2; 14·8 p.c. Al_2O_3	0·206	0·223	0·254	0·266	0·263	—	—	—	Y. Tadokoro
,,	—	—	0·225	—	—	—	—	—	—	Steger
,,	88·8 p.c. MgO; 9·3 p.c. Fe_2O_3	—	—	0·259	—	0·275	—	0·291	0·299	Heyn, Bauer, and Wetzel
,,	87·8 p.c. MgO; 4·7 p.c. CaO; 2·3 p.c. SiO_2	—	—	—	0·265	0·273	0·282	—	—	Green
Zirconia material.	99 p.c. ZrO_2	—	—	—	0·137	—	0·157	0·167	0·175	Bradshaw and Emery
Carbon brick	Coke and tar	—	—	0·312	—	0·358	—	0·377	—	Heyn, Bauer and Wetzel
Chrome brick	31·9 p.c. Cr_2O_3; 8·3 p.c. SiO_2; 24·9 p.c. Al_2O_3; 16·9 p.c. Fe_2O_3	0·172	0·178	0·212	0·221	0·218	—	—	—	Y. Tadokoro
										—

TABLE III.—MEAN THERMAL CONDUCTIVITIES OF REFRACTORY MATERIALS BETWEEN VARIOUS TEMPERATURES.

Material	Composition (main constituents)	App. specific gravity	True specific gravity	Porosity p.c.	Temperature range	Thermal conductivity in C.G.S. units	Diffusivity in C.G.S. units	Remarks	Investigators
Firebrick material	66 p.c. SiO_2; 31 p.c. Al_2O_3	1·94	2·54	23·3	260°–825° 1100°–420° 1350°–510°	0·0029 0·0033 0·0039	—	Fired to Cone 10–11	Dougill, Hodman and Cobb
,,	,,	1·90	2·67	28·7	1005°– ? 1020°– ?	0·00165 0·00120	—	Fired to Cone 8–9	,, ,,
,,	63·2 p.c. SiO_2; 30·4 p.c. Al_2O_3	1·8	—	—	at 400° at 800° at 1000°	0·0014 0·0016 0·0021	—	—	Heyn, Bauer and Wetzel
,,	71·1 p.c. SiO_2; 24·5 p.c. Al_2O_3	1·77	—	—	at 200° at 830°	0·0009 0·0011	—	—	,, ,,
,,	57·9 p.c. SiO_2; 32·9 p.c. Al_2O_3	2·0	2·36	15·9	785°–1030° 892°–1138°	0·00167 0·00206	0·00263 0·00303	Very close structure	Green
,,	72·5 p.c. SiO_2; 23·7 p.c. Al_2O_3	1·91	2·54	24·7	634°–892° 796°–1098°	0·00182 0·00226	0·00322 0·00365	Very close structure	,,
,,	60·8 p.c. SiO_2; 33·9 p.c. Al_2O_3	—	—	—	at 700° at 900°	0·00339 0·00402	0·00820 0·00986	—	Y. Tadokoro
,,	68·0 p.c. SiO_2; 29·0 p.c. Al_2O_3	—	—	—	230°–1160°	0·0035	—	Burnt at 1050°	Wologdine
,,	,,	—	—	—	230°–1000°	0·0042	—	Burnt at 1300°	,,
,,	53·0 p.c. SiO_2; 43·0 p.c. Al_2O_3	—	—	—	at 100°	0·00169	—	—	Boyd Dudley
,,	,,	—	—	—	at 1000°	0·00339	—	—	,,
,,	67·0 p.c. SiO_2; 28·0 p.c. Al_2O_3	—	—	30	0°–1000°	0·00251	—	—	Goerens
,,	Fireclay material	—	—	—	400°–700°	0·00265	—	—	Clement and Egy
Silica material	94·0 pc. SiO_2; 2·0 p.c. CaO	—	—	—	100°–1000° 150°–930°	0·0020 0·0031	—	Burnt at 1050° Burnt at 1300°	Wologdine ,,
,,	95·0 p.c. SiO_2; 1·5 p.c. CaO.	1·75	2·32	24·6	400°–1200°	0·0036	—	Coarse grained	Dougill, Hodsman and Cobb

TABLE III.—*continued.*

Material	Composition (main constituents)	App. specific gravity	True specific gravity	Porosity p.c.	Temperature range	Thermal conductivity in C.G.S. units	Diffusivity in C.G.S. units	Remarks	Investigators
Silica material .	94·0 p.c. SiO_2; 1·78 p.c. CaO	1·51	2·44	38·2	704°–924°	0·00130	0·00286	Fine grained	Green
,,	,,	—	—	—	894°–1142	0·00177	0·00345	—	,,
,,	97·0 p.c. SiO_2; 0·97 p.c. CaO	—	—	—	at 600°	0·0017	—	—	Heyn, Bauer and Wetzel
,,	96·0 p.c. SiO_2; 1·8 p.c. CaO	—	—	—	at 1200°	0·0021			
,,	91·0 p.c. SiO_2; 2·8 p.c. CaO	—	—	—	at 100°	0·0022	—	—	Boyd Dudley
					at 1000°	0·0042			
					at 900°	0·0054	0·0136	—	Tadokoro
Magnesite material	92·0 p.c. MgO; 5·0 p.c. SiO_2	2·40	3·51	31·4	750°–470°	0·0116	—	—	Dougill, Hodsman and Cobb
,,	,,	—	—	—	1370°–690°	0·0091	—	—	,,
,,	86·5 p.c. MgO; 7·0 p.c. Fe_2O_3	—	—	—	450°–830°	0·0135		Fine grained	Boyd Dudley
,,	88·8 p.c. MgO; 9·3 p.c. Fe_2O_3	—	—	—	at 600°	0·0012	—	—	Heyn, Bauer and Wetzel
					at 1200°	0·0014			
,,	87·8 p.c. MgO; 4·7 p.c. CaO	2·56	3·38	24·5	510°–690°	0·00285	0·00352	Close texture	Green
					766°–1097°	0·00255	0·00268		
Carbon brick .	Coke and tar	—	—	—	at 200°	0·0012	—	—	Heyn, Bauer and Wetzel
,, .	—	1·19	1·93	3·8	at 800°	0·0021	—	—	Goerens
Diatomite brick .	—	—	—	—	32°–622°	0·000384	—	—	Griffiths
					64°–939°	0·000461			
Chrome brick .	19·5 p.c. Cr_2O_3; 21·8 p.c. SiO_2; 30·1 p.c. Al_2O_3; 13·7 p.c. Fe_2O_3	—	—	—	at 700°	0·00545	0·00863	—	Tadokoro
		—	—	—	at 900°	0·00477	0·00877	—	,,
Slag wool .	—	—	—	—	74°–352°	0·000197	—	—	Griffiths
					204°–723°	0·000323			

the firing. The sillimanite also increases the refractoriness of the clay. A very good mixture for *sillimanite bricks* is sillimanite with 20 p.c. of ball clay.

Magnesite bricks are composed mainly of magnesia obtained by calcining magnesite. They were made commercially by C. F. Claus in 1868. Their cost is much higher than that of fireclay or silica bricks, but they do work in which the last-named bricks are unsatisfactory. Magnesite bricks are used for lining the bottoms and side-walls just over the slag-line in furnaces producing Thomas and Gilchrist's basic steel. They are also used in ports and blocks, and whenever basic slags are to be resisted at a high temperature. The bottoms and side-walls of many electric furnaces are also built with magnesite bricks. Some cement kilns have also been lined with magnesite bricks.

Magnesite bricks are made from magnesite which has been dead-burned at a very high temperature (*vide* MAGNESITE). The most marked feature in the burning of magnesia is the contraction. The sp.gr. changes from about 3·2 to about 3·7; this corresponds with a contraction of about 15·6 p.c. It is therefore obvious that if magnesite bricks be imperfectly calcined a relatively large contraction will occur near the hot face of the brick, and spalling will result. As in the case of silica bricks, some varieties of magnesite shrink in the kiln more than do other varieties.

The magnesite bricks are made by mixing a small proportion of ground easy calcined magnesia, with ground and graded hard calcined magnesia and the wet mass is moulded, dried, and fired to cone 17–18. The easy calcined magnesia is possibly in a colloidal form, and it thus serves as a binding agent. It does not follow that the purest magnesite furnishes the best bricks. A small proportion of ferruginous impurities seems advantageous. Attempts have been made to add these artificially, in the form of slags, etc. It possibly acts in two ways: (1) by serving as a bond in the fired bricks, and (2) by facilitating the conversion of magnesite from the low sp.gr. form to the high sp.gr. form (possibly periclase). Periclase may be regarded as the equilibrium form of the magnesia in magnesite bricks when in use.

Dolomite, or magnesium limestone, is used in making furnace linings for basic steel process, and in making dolomite bricks. The raw materials should be thoroughly shrunk before use. The bricks are made by processes similar to those employed for magnesia bricks; but, more particularly for linings, the dolomite is mixed with tar or pitch as a binding agent for the raw material. Silica acts as a powerful flux with both magnesia and dolomite, so that a dolomite with over 7 p.c. of silica is generally considered unsafe. If siliceous dolomite be shrunk in shaft-kilns the material may sinter and choke the furnace. The bricks may also disintegrate on exposure to damp air. Attempts to decalcify dolomite and convert it into magnesite have not been successful on a commercial scale.

Zirconia bricks are made in a somewhat similar way. Here again there is a large fire contraction to be dealt with. The mixing and moulding follow methods similar to those employed in making magnesite bricks, but higher moulding pressures are used. The zirconia bricks are even more refractory than the magnesite, and they resist ordinary furnace conditions much better. Their thermal conductivity and coefficient of thermal expansion are low. Silica and clay flux readily with zirconia at high temperatures, so that the raw zirconia, etc., may require treatment to eliminate silica when used for high temperature work. This purification makes the cost fairly high. It is claimed but not demonstrated that the increased life of the zirconia bricks in steel furnaces, etc., more than compensates the additional cost. At about 1800°, in contact with carbon, there is evidence of a reduction of the oxide and the formation of a zirconium carbide.

Thoroughly shrunk, *alumina or bauxite* also promises to give valuable results. Such bricks have a bad name, because the high fire shrinkage of the material has not been eliminated in manufacturing the bricks. Shrunk bauxite, as a kind of artificial corundum, is sometimes used to fortify fireclay bricks. If the material is thoroughly shrunk before use, the results are good.

Chromite bricks are made from ground chromite, maybe without any bond other than mortar, and sometimes with more or less clay, lime, dolomite, magnesite, or tar. After moulding, the bricks are carefully dried and fired. They are chiefly used as a neutral course between acid or basic bricks and fire-bricks. They are also used as linings for copper, antimony, and tin furnaces. With a good grade chromite a refractoriness as high as 2000° may be obtained. Chromite bricks sometimes become soft and spongy in reducing gases and steam.

Bricks are also made from *carbon* with a good type of plastic clay as bond. They are used in the bottoms, sides, and boshes of furnaces used in the manufacturing of iron and steel. A number of other materials have been suggested and used as refractories in a restricted way, *e.g.* iron ore or 'blue billy,' titanium iron ore, carboxides, siloxides, etc.

Literature.—F. Wernècke, Die Herstellung der Feuerfesten Baustoffe, Berlin, 1921; A. B. Searle, Refractory Materials: Their Manufacture and Uses, London, 1917; British Clays, Shales and Sands, London, 1912; F. T. Havard, Refractories and Furnaces, New York, 1912; C. Bischof, Die Feuerfesten Tone, Leipsig, 1904; A. Granger, Fabrication et Emploi des Matériaux et Products Réfractaires, Paris, 1910; H. Ries, Clays, Their Occurrence, Properties and Uses, New York, 1906; Transactions Ceramic Society; Transactions American Ceramic Society.

J. W. M.

REFRIGERATING AND ICE-MAKING MACHINERY. A refrigerating machine is a reversed heat engine in which energy is converted into heat, its function being to take heat from a body below the normal temperature and impart it to a hotter body. According to the second law of Thermodynamics, it is impossible for a self-acting machine unaided by any external agency to convey heat from one body to another at a higher temperature; therefore a refrigerating machine requires the application of energy. In fact, in working from a lower to a higher

temperature an ideally perfect refrigerating machine requires the application of exactly the same quantity of energy as is given off by a perfect heat engine working from the higher to the lower temperature, and the quantity of heat rejected is the quantity of heat taken in at the lower temperature *plus* that due to the added energy. We can therefore define the coefficient of performance of a perfect refrigerating machine working between any two known temperatures.

If Q_1 is the quantity of heat taken in at the lower temperature T_1, Q_2 the heat given out at the higher temperature T_2, and $W = Q_2 - Q_1$ the energy applied, all expressed in thermal units, the efficiency of the process is $\frac{Q_1}{Q_2 - Q_1}$, or in a perfect refrigerating machine $\frac{T_1}{T_2 - T_1}$. This is the ideal efficiency or coefficient of performance for any temperature range, and it is independent of the working substance employed. The following table gives the coefficient for several temperature differences :—

TABLE I.

T_1 Temperature at which heat is rejected in degrees C.	T_2 Temperature at which heat is rejected in degrees C.					
	10	15	20	25	30	35
−20	8·433	7·23	6·325	5·63	5·06	4·61
−15	10·32	8·61	7·38	6·45	5·74	5·16
−10	13·15	10·51	8·766	7·52	6·575	5·85
−5	17·86	13·4	10·72	8·933	7·66	6·7
0	27·3	18·2	13·65	10·92	9·1	7·8
5	55·6	27·8	18·532	13·9	11·12	9·266

It is, of course, not to be expected that such efficiencies are to be obtained in practice. In an actual machine there are many sources of loss, mechanical and otherwise, and allowance must be made for losses due to transmission in taking in the heat and in rejecting it. The very nature of such transmission necessitates a difference of temperature, so that the low temperature produced by a refrigerating machine must be lower and the high temperature higher than the temperature of the body from which heat is to be taken and that of the body to which the heat is to be rejected. This alters the ratio between T_1 and $T_2 - T_1$ and reduces the efficiency.

Two principal types of refrigerating machines are in use at the present time :—

1. That in which atmospheric air is cooled when under compression, and by subsequent expansion in the performance of work.

2. That in which heat is abstracted by the evaporation of a more or less volatile liquid.

In compressed-air machines, which are now little used, ordinary atmospheric air is compressed, and heated by the conversion into heat of mechanical energy expended in compression. The hot compressed air is then reduced in temperature by passing it through a vessel in which cold water is circulated, after which the cooled compressed air is expanded to about atmospheric pressure doing work behind a piston, and is further cooled owing to the conversion of heat into work. There is no change in physical state, and the sensible temperature of the air is raised by compression and lowered by the work done in expansion. For this reason, and owing to the fact that the weight and specific heat of air are so low, the difference between T_1 and T_2 is very great. Moisture in the air influences the final temperature owing to the heat given off in condensation and freezing. With this type of machine refrigeration is generally effected by discharging the cold air directly into the room or vessel to be cooled ; but sometimes the air is used in a closed circuit, the cooled air being passed through pipes placed in the room, and then taken back to the machine to be used over again. In either case the cooling effect is produced by the actual heating of the expanded and cooled air, and owing to the high temperature of the compressed air in relation to the temperature of the cooling water and the low temperature of the discharged air in relation to the temperature of the room, the coefficient of performance is very low. Were it practicable to construct and apply compressed-air machines dealing with very large volumes of air without undue losses, so that the final temperature of the compressed air is only slightly above that of the cooling water and the temperature of discharged air only slightly below that desired to be produced, we should then have efficiencies approximating to those given in Table I. In practice the air is compressed to about 50 lbs. above the atmosphere and discharged at a temperature approaching 149°C. (300°F.). It then passes through coolers, where it is reduced to within about 3°C. (5·4°F.) of the initial temperature of the cooling water and is deprived of a portion of its moisture, and is then expanded behind a piston to a little above atmospheric pressure and discharged at a temperature of about −57°C. (−70°F.). The compression and expansion pistons are connected, and the difference in power expended in compression and that given back in expansion, *plus* friction, is supplied by a steam-engine or any other source of power.

In the second class, for many years small hand-worked machines have been made, in which the evaporation of water under a high vacuum is employed ; and the same machine, but on a large scale and using a vacuum produced by a steam ejector, has been successfully applied for the cooling of magazines and for other purposes in which a comparatively high temperature is required. For industrial purposes, however, although it is theoretically possible to work with any liquid, practically all machines of this type work either with ammonia (NH_3), carbon dioxide (CO_2), or sulphur dioxide (SO_2), as the refrigerating agent. Of these ammonia is most largely used, because, owing to its physical properties, it gives the greatest heat elimination for a given expenditure of power. In all cases heat is abstracted by evaporation of the agent, the vapour being compressed and condensed, and the liquid used over again. Ammonia machines are also made in which the vapour is absorbed by water, which is subsequently heated and the ammonia evaporated off and condensed. These are respectively known as ‘ compression ’ and ‘ absorption ’ machines.

A diagram of a compression machine is shown in Fig. 1. There are three principal parts: refrigerator or evaporator, compressor, and condenser. The refrigerator usually consists of a coil or a series of coils connected at one end with the suction of the compressor, the delivery from the compressor being connected with the condenser, which also consists of a coil or series of coils. The refrigerator coils are surrounded with the substance to be cooled, and around the condenser coils cooling water is circulated. The bottom of the condenser coils is connected to the refrigerator coils by a pipe in which is a valve for regulating the quantity of liquid passing from the condenser to the refrigerator. The machine being in action, the refrigerating liquid flows into the refrigerator, in which the pressure is maintained so as to give the desired temperature of evaporation, and as this temperature is always below the temperature of the substance outside the coils, heat passes in from the outside, and causes the liquid to evaporate at the temperature T_1, the vapour being continually drawn off by the pump which compresses and delivers it into the condenser at the temperature T_2, which is somewhat

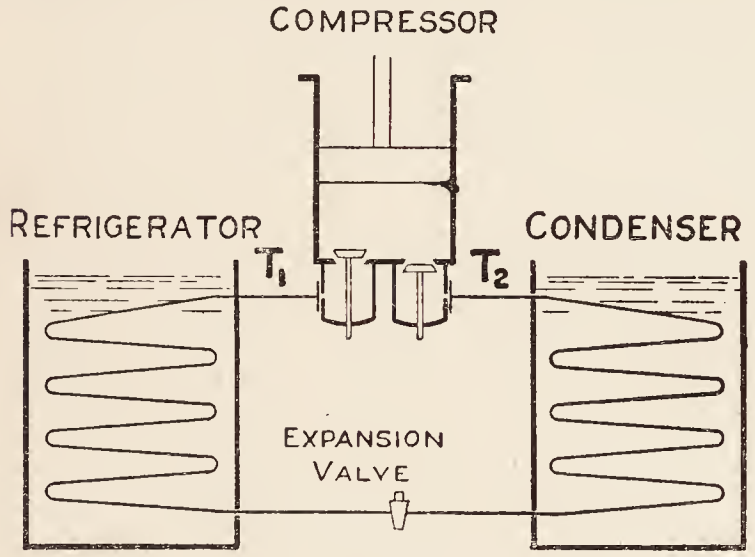


FIG. 1.

above that of the cooling water. In the condenser heat passes from the compressed vapour into the water, the vapour being condensed, and the liquid which collects at the bottom returns through the regulating valve into the refrigerator. It will thus be seen that the essential difference between a compressed-air machine and a machine using a condensable vapour is that, in the one case, heat is taken in and rejected by raising and lowering the sensible temperature of the air; and, in the other, the heat is taken in and rejected at constant temperature during the change in physical state of the agent. Consequently the results obtained with a vapour-compression machine must approach the ideal coefficient of performance much more nearly than those obtained with an air machine. By properly arranging the surfaces in refrigerator and condenser there need not, as a rule, be more than about 6°C. (11°F.) difference between the temperature of evaporation and that of the liquid to be cooled, and between the temperature of condensation and that of the cooling water leaving the condenser; but these differences depend on the design and construction of the parts. In cooling insulated rooms the difference between the temperature of the air and the evaporating liquid is usually about 8°C. (15°F.).

Referring to Fig. 1, it will be seen that the liquid passes from the higher pressure and temperature of the condenser to the lower pressure and temperature of the refrigerator without performing external work, and in this respect the cycle differs from that of a reversed perfect heat engine. The liquid enters the refrigerator at condenser temperature, and before any useful refrigerating work can be performed it must be reduced to the refrigerator temperature by the evaporation of a part of its own quantity. The amount of this lost work is dependent on the relation between the latent heat of evaporation and the specific heat of the liquid, and varies according to the liquid used. It is smaller in ammonia than in carbon dioxide and sulphur dioxide, and it is largely for this reason that machines employing ammonia are so much used. Also with carbon dioxide, which has a critical temperature of 31·4°C. (88·4°F.), the loss increases rapidly as the cooling water temperature rises, and beyond the critical temperature the cooling effect in the refrigerator is not produced under constant temperature, but by the actual heating of the vapour which on its way from the condenser has been cooled by the performance of internal work in expanding through the regulating valve from condenser to refrigerator pressure. The critical point of ammonia is 136°C. (276°F.), a temperature never approached in refrigerating machines, so that when the plant is properly charged ammonia always enters the refrigerator in the liquid form. In cooling brine to −7°C. (20°F.), and with cooling water at 15·5°C. (60°F.), a well-designed compression machine of medium size driven by a steam-engine using 7 kilos. of steam per I.H.P. hour will abstract about 316 calories per kilo. of steam (575 B.T.U. per pound). The same machine driven by a gas-engine and suction gas plant would abstract about 5800 calories per kilo. of anthracite.

In absorption machines ammonia is the refrigerating agent, but there is no compressor. The vapour from the refrigerator passes over or through cold water which absorbs it, and the liquid is then pumped into a vessel in which it is heated by steam, and the ammonia driven off into the condenser. A complete absorption plant consists of a generator containing tubes to which live or exhaust steam is supplied at suitable pressure according to the temperature of the condensing water, an analyser, a rectifier, a condenser, a refrigerator, an absorber, and a pump for forcing the strong liquor produced in the absorber back through a heat interchanger into the analyser, where, meeting with the vapour rising from the generator, the ammonia is driven off, the water falling back into the generator. The process is thus carried on continuously. The condenser and refrigerator may be of precisely similar construction to those of a compression machine, the difference lying entirely in the mode of recovering the ammonia. In an absorption plant the only moving part is the strong liquor pump. In evaporating the ammonia, the latent, as well as part of the sensible heat of the steam is utilised in the generator, but much heat is required on account of having to drive off the ammonia from the water by which it has been absorbed, each kilo. requiring about 462 calories, whereas the latent

heat of ammonia at the condenser temperature is only about 297. The coefficients of performance as given in Table I. are not applicable to absorption machines, and in estimating their efficiency it is usual to take the ratio between the heat given off by the steam condensed in the generator and that abstracted in the refrigerator. One kilo. of exhaust steam supplied to a generator of an absorption plant will abstract about 280 calories in the refrigerator when cooling brine to −7°C. (20°F.) and with cooling water at 15·5°C. (60°F.).

Refrigerating machinery is used for the production of ice, for the preservation of perishable foods in cold stores on land and on board ship, and for cooling liquids and gases. The application is the same in compression and absorption machines. Ice is sometimes made by freezing the water on coils and surfaces in which the refrigerating agent is evaporated, but more generally the machine in the first instance cools an uncongealable brine, which is circulated through or around the freezing plates or cans. If clear ice is desired, the water must be agitated during freezing, or distilled water must be used. For the cooling of stores the air may be directly cooled by pipes called direct expansion pipes, in which ammonia or other liquid is evaporated, or by pipes through which cold brine is circulated, or by a circulation of air previously cooled in a special cooler.

One of the earliest applications of refrigerating machinery was for the separation of paraffin from shale and other oils, the oil containing paraffin in solution at ordinary temperature being passed over cold surfaces, which caused the paraffin to crystallise out. In the same way naphthalene and other substances can be separated from gases, and by having two or more supplies of the cooling agent at different temperatures any gas can be subjected to fractional condensation. Oils are artificially cooled and treated in filter presses to separate the stearin. In the manufacture of margarine very rapid cooling and separation of the residual milk is essential. The dry process in which the liquid margarine passes on to a revolving drum cooled by brine is now superseded to a large extent by the use of a plentiful supply of cold water applied in the form of a jet, so that the stream mixes intimately with the hot liquid margarine and immediately cools and washes it.

In the manufacture of potassium chlorate, the residual liquor which was formerly allowed to run to waste is now cooled to a temperature of about −26°C. (−15°F.), and a large proportion of the chlorate is recovered. The liquid is cooled in a tank by direct contact with expansion pipes, the crystals falling to the bottom. The cold liquor after treatment passes through an interchanger and partially cools the new charge on its way to the crystallising tank. There are many other applications of refrigerating machinery for assisting crystallisation (carbolic acid, for instance), and some years ago an attempt was made to use it in the crystallisation of common salt in place of the evaporation process. In the ammonia soda process refrigeration is employed to separate ammonium chloride from the liquor. In each case the actual cooling surfaces must be arranged to suit the material to be cooled, and, when possible, it is of course economical to cool the new charge by the cold spent liquor. In beet sugar manufacture to increase the yield it is customary to use caustic strontia to form strontium saccharate, which is separated by filtration from the molasses. On cooling the strontium saccharate to about 5°C. (40°F.) it is split up into sugar and caustic strontia, the latter being used over again. The manufacture of the most important class of aniline dyestuffs, the azo- colours, is largely dependent upon refrigeration. In the explosives industry, refrigeration finds application in checking chemical reaction and spontaneous decomposition, to which many nitro explosives are subject at high temperature. Other applications of refrigeration are in the liquefaction of chlorine which at atmospheric pressure requires a temperature of about −40°C. (−40°F.), and the cooling of viscose in the manufacture of artificial silk. In brewing and many other industries large quantities of cold water are required, and in most instances refrigerating machinery is used. Refrigeration is also used in controlling the fermentation of beer, yeast, tobacco, cheese, cream, and other substances, and in drying air. In the mercerising process it has been found advantageous to cool the caustic alkalis. The Hoepfner process of producing pure sodium sulphate by crystallisation from acid solutions necessitates the use of brine at a temperature of about −4°C. (25°F.), and in the same process large quantities of chlorine are produced in the electrolytic production of zinc, the chlorine usually being condensed by means of a refrigerating machine.

Liquid air, oxygen, nitrogen, and hydrogen are also produced by means of low temperatures, but the apparatus employed differs from those considered in this article, and is dealt with under a separate heading.

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T. B. L.

REGINA PURPLE. *Acetate of o-tolyl-p-rosaniline* $C_{28}H_{25}N_3O_4$ *v.* TRIPHENYLMETHANE COLOURING MATTERS.

REGULUS. An alchemistic term signifying *the little king*, apparently first applied to antimony. Now used in metallurgy to denote an impure metal obtained from its oxide or sulphide by fusion with a reducing agent.

REHEATING. A metallurgical term mainly applied to the operation of heating puddled bars to a welding heat preparatory to passing them through rolls.

REICHARDTITE. A massive variety of epsomite, $MgSO_4,7H_2O$, found in the Stassfurt

salt deposits (Krause, Arch. Pharm. 376, 41), *v.* EPSOMITE.

RENADEN *v.* SYNTHETIC DRUGS.

RENOFORM *v.* SYNTHETIC DRUGS.

RESACETOPHENONE *v.* KETONES.

RESALDOL. Syn. for resorcyl benzoic acid ethyl ester.

RESAZURIN (*Azoresorcin*, *Diazoresorcin*, *Resazoin*). An indicator which gives a blue colour with alkalis and a red with acids.

It is prepared by dissolving 4 grms. resorcinol in 300 c.c. dry ether and adding 3–4 c.c. of fuming nitric acid (sp.gr. 1·25), the temperature being kept at −5° to −8°. The solution is allowed to stand in a cool place for two days and the dark-coloured crystals separated from the mother liquor and washed with ether and water until the washings have a pure blue colour (Crismer, Bull. de l'Assoc. Belg. des Chimistes, 10, 22; J. Soc. Chem. Ind. 1896, 618).

Resazurin occurs in reddish-brown crystals, slightly soluble in water, more soluble in alcohol, and easily soluble in ethyl acetate. It is a monobasic acid, but its exact composition is unknown.

It is prepared for use by dissolving 0·2 grm. in 40 c.c. of N/10 ammonia and diluting to 1000 c.c. The solution has a deep blue colour by reflected light, but is reddish by transmitted light; it is quite stable. About 3 drops of this solution suffice for the titration of 200 c.c. of liquid.

Resazurin is specially useful for titrating N/10 solutions of borax, to which litmus or phenol-phthalein is not sufficiently sensitive, and is generally very sensitive to alkalis. It cannot be used for nitric acid or weak organic acids (*see* Lemoine, Bull. Assoc. Belg. Chim. 13, [4] 178, 185, 188; and 187; J. Soc. Chem. Ind. 1899, 608, 610, 611, 614).

RESINATE LAKES. These lakes are prepared by dissolving 100 parts of pale-coloured resin in a solution of 33 parts of soda crystals in 1000 parts of water. The mixture is boiled for an hour, after which it is cooled down to about 50° by the addition of 1000 parts of cold water, and then the filtered solutions of such basic dyes as magenta, methyl-violet, brilliant green, auramine, &c., are added. The amount of dye used depends on the depth of colour desired, and varies between 5 and 15 p.c. on the amount of resin. The resin-soap solution must be of the right temperature and degree of concentration when the addition of dye is made, so as to avoid the separation of the colour bases in the form of resinates. A slight excess of a dilute solution of a metallic salt is added; in the case of zinc sulphate, 55 parts dissolved in 1000 parts of water are used for the above quantities of resin, &c. The solutions of magnesium salts must be very dilute, since otherwise the lake becomes resinous on drying. The lakes which are not to be used in the paste form are thoroughly dried at a temperature of 40° to 50°, or 70° in the case of magnesium lakes. The dried lakes are of an exceedingly fine bright colour. They are not affected by air or moisture, and boiling water fails to extract colouring matter. Weak alkalis and acids are also without action, and strong solutions of hypochlorites act very slowly on them, provided that light is excluded; but, in presence of light, oxidising agents act rapidly. Their solubility in alcohol depends upon the nature of the combined metallic base; magnesium lakes dissolve easily, calcium and barium lakes fairly easily, aluminium and iron lakes only slightly. Benzene, ether, chloroform, light petroleum, and other solvents dissolve them easily. Some of the lakes—those of aluminium, for instance—are decomposed when their solutions are kept for a little time, the metallic base separating, but others, such as those of zinc and calcium, keep indefinitely. They resist light fairly well. Lakes made with brilliant green resist badly, but those coloured with auramine, methyl-violet, safranine, chrysoidine, and particularly rhodamine, resist very well. The colours bleach more easily when in combination with aluminium and chromium than with zinc and magnesium. The action of light renders the lakes insoluble in benzene, liberating the colour-base, which may be extracted with hot water. The solutions of the lakes form good varnishes, whose elasticity and power of endurance are increased by the addition of a little india-rubber or gutta-percha. The following is an example of such a varnish: 30 parts of magnesium lake are dissolved in 80 parts of benzene and 20 parts of chloroform, and the solution obtained mixed with 150 parts of a clear solution of $1\frac{1}{2}$ p.c. of india-rubber in chloroform and benzene (A. Müller-Jacobs, Dingl. poly. J. 273, 139; J. Soc. Chem. Ind. 8, 770).

RESINS. Resins constitute a class of vegetable, or, rarely, animal products which are solid or, semi-solid, insoluble in water, but generally soluble in alcohol, ether, and volatile oils. They nearly all begin to soften at temperatures much below their melting-points. They are often left by the spontaneous evaporation of oleoresinous juices which exude either naturally or by incision from the trunks of trees. A number are found as minerals, but these are undoubtedly the products of extinct vegetation. Others are extracted from various parts of plants by such solvents as alcohol and ether. This article excludes those resins which contain benzoic or cinnamic acid (*balsams*), those which appear in commerce admixed with gum (*gum resins*) or volatile oil (*oleo-resins*), and those which consist of hydrocarbons allied to *petroleum*. It is perhaps to be regretted that it is necessary to retain such a classification as this, based as it is upon commercial or botanical considerations, or at best upon physical distinctions of solubility. Chemical inquiry, however, has not been carried far enough yet to make a more scientific arrangement possible, and indeed, so widely do the various resins that have been studied differ from one another chemically that it seems likely that as a class they will ultimately disappear, being taken to fill in gaps here and there in the growing structure of organic chemistry. For the relation between ability to form resins and chemical constitution, *see* W. Herzog and J. Kreidl (Zeitsch. angew. Chem. 1923, 36, 471–473).

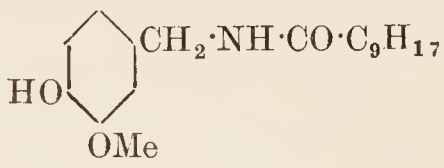
We shall here treat of the more important representatives of this group of substances. For those which are less known, see the various Reports on Botanical Economics, and Museum Catalogues. On the formation of resins see Heldt (Annalen, 63, 48), Wiesner (Sitz. Ber. K. Akad. Wien. 52, 2, 118), Barth (Zeitsch. Chem. 1867, 508), and Tschirch (Arch. Pharm. 243,

81); their composition and behaviour towards reagents, Rose (Annalen, 13, 174), Johnston (*ibid.* 44, 328); the compounds formed by the action of melted potassium hydroxide, Hlasiwetz and Barth (*ibid.* 134, 265; 138, 61; 139, 77); their neutralisation or saponification coefficients when treated with a standard solution of caustic alkali, Kremel (Zeitsch. anal. Chem. 26, 262; Pharm. J. [iii.] 17, 547); their respective iodine absorption numbers, Williams (Chem. News, 58, 224); determination of their methoxyl equivalents, Bamberger (Monatsh. 11, 84), and on the systematic identification of resins, see Hirschsohn (Pharm. Zeit. 16, 81; 24, 529; Zeitsch. anal. Chem. 17, 256); Dieterich (Pharm. Zeit. 37, 424), and Schmidt and Erban (Monatsh. 7, 665). See also Tschirch, Die Harze und die Harzbehälter, Leipzig, 2nd ed. 1906; and Allen's Commercial Organic Analysis, 4th ed. vol. iv. 1911; vol. ix. 1917.

Alouchi, or **Aluchi Resin.** A resin imported from Madagascar. It is friable, dirty-white externally, blackish and marbled within, and has a bitter, peppery taste. It was examined by Bonastre (J. Pharm. Chim. 9, 180; 10, 1), who found it soluble in cold alcohol to the extent of 68·12 p.c. A further portion, 20·45 p.c., dissolved in hot alcohol. It contains a small proportion (1·6 p.c.) of essential oil. *V.* also Vauquelin (Ann. Chim. ii. 72, 299).

Arnica Resin, *Arnicin.* The rhizome of *Arnica montana* (Linn.), a compositous plant inhabiting the northern and central regions of Europe and America (Bentl. a. Trim. 158), was deleted from the B. P. in 1914; *Arnica* U.S. P. refers to the dried flower heads only. Both rhizome and flowers contain a resinous substance to which the name *arnicin* has been given, together with *gum*, *wax*, *inulin* 10 p.c., *volatile oil*, and an alkaloid (?) *arnicine* (Bastick, Pharm. J. 10, 386), and other constituents. The resinous compound arnicin was isolated by Walz (Neuer. Jahresb. Pharm. 13, 175; 14, 79; 15, 329). See further B. Börner (Diss. Erlangen, 1891), and Klobb (Compt. rend. 1904, 138, 763; 1905, 140, 1700); the latter isolated the phytosterol arnisterol $C_{28}H_{46}O_2$.

Capsicum Resin. The fruits of *Capsicum minimum* (Roxb.) (*Capsici fructus* B. P.; *Capsicum* U.S. P.) and *Capsicum annuum* (Linn.), constituting respectively the small and large red or cayenne pepper pods of commerce (chillies), yield a *resin* to which the acrid property of the pods was once attributed. The other important constituents are a *volatile oil*, a volatile alkaloid, *capsicine*, which resembles coniine (Felletár, J. Pharm. Chim. 1870, 347; Thresh, Pharm. J. [iii.] 6, 941), and an intensely active acrid, crystalline compound discovered by Thresh, *capsaicin*, to which the pungency of cayenne pepper is now ascribed (*ibid.* [iii.] 7, 21, 259, 473; 8. 187). *V.* also Meyer (Pharm. Zeit. 1889, 130), Pabst (Arch. Pharm. 230, 108), Nessler (Zeitsch. Nahr. Genussm. 11, 661), Micko (*ibid.* 1898, 818; 1899, 411), Nelson (J. Ind. Eng. Chem. 1910, 2, 419), Lapworth and Royle (Chem. Soc. Trans. 1919, 115, 1109). Capsaicin has the formula—



Nelson (J. Amer. Chem. Soc. 1919, 41, 1115) concludes that capsaicin is a condensation product of vanillylamine and a decylenic acid $C_{10}H_{18}O_2$. It possesses feebly basic properties and crystallises from a mixture of light petroleum and ether in monoclinic plates. It melts at 64·5° (Nelson), sublimes at 115°, and has a sp.gr. of 1·060. Most solvents, including sulphuric and glacial acetic acids, dissolve capsaicin; but it is insoluble in water, and is thrown out of its solution in alkalis by a stream of carbon dioxide. The fruits of *Capsicum minimum* (Roxb.) contain about 20 times as much capsaicin as those of *Capsicum annuum* (Micko, *l.c.*).

Castoreum Resin. The dried preputial follicles of the beaver, *Castor fiber* (Linn.), have been used in medicine as a nervous stimulant or antispasmodic (Pereira, Mat. Med. 1853, 2, 2266), they are not included in the B. P. or U.S. P. Castor contains a *resin*, 1–2 p.c. of *volatile oil*, and a neutral crystalline substance, *castorin*, apparently related to cholesterol (Bizio, Arch. Pharm. 11, 112; Valenciennes, Pharm. J. 1861, 329). If castor be treated with hot alcohol, either with or without previous admixture with lime, a solution results which, on cooling, deposits castorin in crystals, and from the mother-liquor of which the resin may be obtained by the addition of water. The resin (14–58 p.c.) is nearly black and possesses the bitterness and acridity of castor in a high degree.

Colophony (*Common Resin*; *Rosin*; *Resina*, B. P.; *Rosin*, U.S. P.; *Colophane*, Fr.; *Colophonium*, Ger.). Colophony is the residue which remains after the volatile oil has been removed by distillation from the oleoresins, the crude turpentines which exude from various species of coniferæ. It varies somewhat, according as it is derived from the one or the other species, and with the method employed for its production. The browner resins are mostly of American origin, from *Pinus palustris* (Mill.); whilst those of a lighter colour come by way of Bordeaux, being the yield of *Pinus Pinaster* (Solander), found in the districts of the Landes and the Gironde. It varies in colour from pale amber to dark red-brown. The 'white resin' of commerce owes its light-yellow colour to a slight opacity, due to the presence of small quantities of water.

Colophony is a very brittle solid with a glassy fracture. It has a faint odour of turpentine, and scarcely any taste. It is heavier than water, in which it is insoluble. Its sp.gr. is generally 1·07 to 1·08. Ether, chloroform, acetone, benzene, volatile and fixed oils dissolve it readily, and at 60° it is soluble in its own weight of alcohol or glacial acetic acid. It is soluble in alkalis. Acid number 150–180 and practically identical with saponification number. It softens at 80°, and melts variously from 100° in some specimens to 135° in others. Heated to higher temperatures it yields gaseous products and a distillate of *resin oil*, but in a current of steam above 200° colophony may be distilled without any appreciable change.

E. Knecht's (J. Soc. Dyers and Col. 1923, 39, 338–340) previous conclusion that rosin consists mainly of anhydrides (Knecht and Hibbert, J. Soc. Chem. Ind. 1919, 472 A) of the

formula $(C_{20}H_{29}O_2)_2O$ is defended and additional evidence adduced in favour of this contention. The *l*- and *d*-acids of m.p. 161°C. obtained from rosin by repeated recrystallisation and further purified were heated in a current of carbon dioxide. The presence of water in the cool parts of the tube was evident when the temperature had reached 145°C., and about one-half of the acid (both *d*- and *l*-acids) was found to have melted. The indefinite melting-points of rosin acids is, therefore, ascribed to the formation of anhydrides (J. Soc. Chem. Ind. 1923, 42, 1234 A).

American colophony consists essentially (85–95 p.c.) of a resin acid, *abietic acid* $C_{20}H_{30}O_2$ (=sylvic acid) (Maly, Annalen, 149, 115, 161, 244; Liebermann, Ber. 17, 1884; Haller, *ibid.* 18, 2165; Mach, Monatsh. 14, 186; 15, 627; Fahrion, Zeitsch. angew. Chem. 14, 1197, 1221, 1252; Levy, *ibid.* 18, 1739; Ber. 39, 3043). Varying figures for the melting-point of abietic acid have been given, mostly about 155°; Levy, by vacuum distillation and repeated crystallisation from methyl alcohol, obtained a product melting at 182°.

The acid potassium salt (Mach) and some others are crystalline (Ellingson, J. Amer. Chem. Soc. 1914, 36, 325). For constitution of abietic acid, *see* Easterfield and Bagley (Chem. Soc. Trans. 1904, 85, 1238), Tschirch and Studer (Arch. Pharm. 1903, 241, 405), Fahrion (Zeitsch. angew. Chem. 1907, 20, 356), Endemann (Amer. Chem. J. 1906, 33, 523), Pooth (Farbenzeit. 1915, 20, 1056). For colloidal properties of the acid and its ammonium salt, *see* Cohn (Chem. Zeit. 1906, 40, 791).

When colophony dissolves in alkali, an alkaline abietate, or *resin soap*, is formed. This is largely employed as an admixture in the manufacture of the commoner soaps. Heated to redness colophony evolves a mixture of gases, which burns with a bright flame, and it has been proposed as a source of illuminating gas. It enters largely into the constitution of the less-esteemed varnishes; esters and metallic resinates of calcium, barium, strontium, and zinc are used. Resinate driers are the salts of lead and of manganese. It is used for the caulking of ships, for cements, as a flux in the soldering of metals, and in pharmacy it enters into many ointments and plasters, particularly for veterinary use. The soluble salts are used for sizing paper.

The *resin* or *rosin oil* obtained by the dry distillation of resin is widely made use of, and its chemical constituents are being more and more studied. It consists essentially of a mixture of hydrocarbons and fatty acids. Generally it is separated into two portions, the lighter spirit that first comes over being collected apart from the heavier oil, which distils last. The lighter spirit is used as a substitute for oil of turpentine, while the heavier is employed as a lubricant and in soap-making. The lighter *resin spirit*, boiling below 330°, contains, according to Renard (Ann. Chim. [vi.] 1, 223), the following compounds: pentane, boiling from 35° to 38°, amylene (35°–40°), the hydrocarbons C_6H_{14} (64°–66°) and C_6H_{12} (67°–70°), hexahydrotoluene (95°–98°), tetrahydrotoluene (103°–105°), toluene (111°), hexahydroxylene (120°–123°), tetrahydroxylene (128°–130°), xylene (136°), hexahydrocumene (147°–150°), the hydrocarbon C_9H_{16} (155°?), cumene (151°), terpenes (154°–157° and 171°–173°), hexahydrocymene (171°–173°), cymene (175°–178°), *m*-ethylpropylbenzene (193°–195°), the hydrocarbon $C_{16}H_{28}$ (about 260°), *iso*butyric aldehyde (60°–62°), valeric aldehyde (96°–98°), also *iso*butyric acid and valeric acid. Colophene (318°–328°), the compound formed by polymerising turpentine oil by means of sulphuric acid, is also a constituent of resin spirit (Deville, Annalen, 37, 193). There is little doubt that the colophene found in resin spirit by Deville is identical with *abietene* $C_{18}H_{28}$, a hydrocarbon obtained by Easterfield and Bagley (Chem. Soc. Trans. 85, 1244) by the distillation of crystalline abietic acid. The heavier *resin oil*, boiling above 300°, consists of hydrocarbons together with a mixture of acids and phenols and much undecomposed colophony. For other constituents of resin oil, *see* Tilden (Ber. 13, 1604), Kelbe (Annalen, 210, 12), Kelbe and Lwoff (Ber. 16, 351), and Lwoff (*ibid.* 20, 1020), Brownsword and Cohen (J. Soc. Chem. Ind. 1890, 16), Tschirch and Wolff (Arch. Pharm. 245, 1), and particularly Schultze (Annalen, 1908, 359, 129). The gases evolved during the distillation have been examined by Schiel (*ibid.* 115, 96). When the resin oil boiling from 103°–104° is allowed to stand in contact with air and water, a crystalline solid, *colophonium hydrate* is formed, having the composition $C_{10}H_{22}O_3,H_2O$. It melts at 106° and sublimes with some decomposition (Tichborne, Pharm. J. [iii.] 1, 302; Anderson, J. 1869, 787; Tilden, Ber. 13, 1604). According to Bischoff and Nastvogel (*ibid.* 23, 1919), the breaking up of colophony by destructive distillation is much simpler if the operation be performed under reduced pressure. In this case the products are chiefly two: one a hydrocarbon, $C_{20}H_{32}$, boiling at 218°–220° (30 mm.), which is probably colophene; the other, a liquid, which slowly solidifies to a mass of microscopic crystals having the composition $C_{40}H_{58}O_3$. This compound is, however, found by Easterfield and Bagley to be ordinary abietic acid, melting at 160°–165°. The distillation of colophony in superheated steam yields the same products as the distillation under reduced pressure.

When resin is distilled with lime, another series of compounds is produced (Fremy, Ann. Chim. [ii.] 59, 13; Bruylants, Ber. 8, 1463; 11, 448). For distillation of resin with sulphur, *v.* Currie (J. 1874, 921), Kelbe (Chem. Zentr. 1887, 1504), Vesterberg (Ber. 36, 4200); for products of the oxidation of resin with nitric acid, *v.* Schreder (Annalen, 172, 93) and Vogel (J. 1869, 785), and for distillation of colophony and resin oil under pressure, *v.* Kraemer and Spilker (Ber. 32, 2952, 3614; 33, 2265).

For methods of detecting the presence of resin oil in fixed, volatile or mineral oils, *see* Allen's Commercial Organic Analysis, 4th ed. vol. iv. 38–47, and Storch (J. Soc. Chem. Ind. 7, 136), Holde (*ibid.* 7, 526; 9, 419), Morawski (*ibid.* 8, 572), Chenevier (*ibid.* 9, 825), Baudin (J. Pharm. Chim. [v.] 23, 279), Gilbert (Chem. Zeit. 13, 1428), Grittner (Zeitsch. angew. Chem. 5, 265), Zune (Compt. rend. 114, 490), McIlhiney (J. Amer. Chem. Soc. 16, 385), Klimont (Chem. Zentr. 1895, i. 563), Cornette (L'Orosi, 19, 234), De Koningh (Chem. News,

77, 287), Halphen (J. Pharm. Chim. [vi.] 16, 478), Valenta (Chem. Zeit. 29, 807).

Resin is used largely as an adulterant. For methods for its detection and estimation, *see*— Resin in Soap: Senier (Amer. J. Pharm. [iv.] 4, 353), Gladding (Amer. Chem. J. 3, 416), Heiner (J. Pharm. Chim. [v.] 11, 434), Wright and Thompson (Chem. Soc. Proc. 2, 175), Grittner and Szilasi (Chem. Zeit. 10, 325), Morawski (J. Soc. Chem. Ind. 1888, 891; 1889, 592; Chem. Zeit. 12, 1321), Holde (J. Soc. Chem. Ind. 1889, 592), Twitchell (*ibid.* 1891, 804), Lewkowitsch (*ibid.* 12, 503), Landin (Chem. Zeit. 21, 25). Resin in Fats: Gladding (Amer. Chem. J. 3, 416), Focke (Chem. Zentr. 1886, 44), Landin (Chem. Zeit. 21, 25), Holde (Zeitsch. angew. Chem. 15, 650). Resin in Wax: Morawski (*l.c.*); Röttger (Chem. Zeit. 15, 45). For a method of testing colophony, *v.* Dieterich (Zeitsch. angew. Chem. 12, 915).

A considerable change occurs in the composition of powdered resin when the material is stored in partially filled corked bottles; this change (in the analytical characters) is noticeable within one week, continues at a significant rate for three weeks, and is not complete at the end of six weeks. For example, in six weeks there is a decrease of 5·3–9·3 in the acid value, and 47·3–52·2 in the iodine value, an increase of 5·1–8·9 in the saponif. value, and a rise of 8·9°–11·3°C. in the melting-point. It is therefore important that samples of resin should not be powdered until immediately before the analysis is commenced (F. P. Veitch and W. F. Sterling, Ind. Eng. Chem. 1923, 15, 576–577; J. Soc. Chem. Ind. 1923, 42, 1186, A.).

Common Frankincense (*Gum Thus*; *French Pine Resin*; *Galipot*, Fr.). The crude turpentine which concretes on the trunks of the French pine trees was scraped off and employed in pharmacy. The greater part of the *Gum Thus* of commerce is now, however, derived from the American pine trees, *Pinus palustris* (Mill.) and *Pinus Taeda* (Linn.) (*Thus americanum*, B.P.; *Terebinthinum*, U.S. P.). The French resin does not consist of abietic acid but of a group of nearly related pimaric acids. These have been investigated by Laurent (Ann. Chim. [ii.] 72, 34; [iii.] 32, 459), Maly (Annalen, 129, 94; 132, 253), Duvernoy (*ibid.* 148, 143), Strecker *ibid.* 150, 131), Bruylants (Ber. 11, 448), Caillot (Bull. Soc. chim. [ii.] 21, 387), Liebermann (Ber. 17, 1884), Haller (*ibid.* 18, 2165), Vesterberg (*ibid.* 18, 3331; 19, 2167; 38, 4125; 40, 120), and by Henry (Chem. Soc. Trans. 79, 1151). For investigations of the natural resins, *see Turpentine* in article on OLEO-RESINS.

Copal Resin. Copal is the concrete exudated juice of various trees. It is obtained either directly from the trees or as a fossil resin buried in the earth in their neighbourhood. Fossil copal is a highly-prized variety. Copal comes from the East Indies, South America, New Zealand, and both the east and west coasts of Africa. Some copals are soft; these are obtained from Sumatra, Java, Molucca, the Philippines, and Australia, and they are soluble in ether. The hard copals, which do not dissolve in ether until they have undergone a chemical change, come by way of Calcutta from Zanzibar and the African coast, and by way of Bombay from Madagascar, Mauritius, and Bourbon. Hard copal varies in properties somewhat with the origin of the different resins which are known by that name; but generally it is of a light-yellow or brown colour, without taste or smell, and has always been prized for varnishes. It occurs in roundish or flattish pieces, more or less transparent, and breaks with a conchoidal fracture. The sp.gr. varies from 1·04 to 1·14, but generally it is below 1·07. In the crude state hard copal is insoluble in alcohol, and only partially soluble in ether or oil of turpentine. When, however, the crude resin is heated, gases are evolved, and a residue remains which dissolves readily in ether and oil of turpentine. In making varnishes, copal is melted and heated slightly, and hot turpentine slowly run into the melted resin.

Submitted to destructive distillation, copal yields a terpene boiling at 160°–165° and a heavier oxygenated oil (Schibler, Annalen, 113, 339). Friedburg (J. Amer. Chem. Soc. 12, 285, 392) finds that when copal is distilled, a terpene, probably limonene, comes over between 100° and 185°, and that above that temperature decomposition takes place until at 215° a dark residue remains. Wallach and Rheindorff (Annalen, 217, 308) find pinene and dipentene to be present in the oily distillate obtained by the dry distillation of copal.

Manilla copal is exported from the Philippine Islands. Much of the copal, however, which comes from the Philippines is produced in the Dutch East Indies and certain islands in Polynesia; but, in recent years, the greater part of the resin collected in the Dutch East Indies has reached European markets through Singapore and other ports and is known in commerce as 'Macassar,' 'Pontianac,' or Singapore copal. These copals are almost entirely obtained from the *Agathis loranthifolia* (Salisb.). They have been investigated by Tschirch and Koch (Arch. Pharm. 240, 202) and by Richmond (Philippine J. Sci. 1910, [A] 5, 177). Analytical constants are given by Coffignier (Bull. Soc. chim. [iv.] 3, 453), and the products obtained by destructive distillation and by oxidation have been investigated by Brooks (Philippine J. Sci. 1910, [A] 5, 203, 219).

For methods for determining the solubility of Manilla copals in alcohol, *see* F. Simion (Chem. Zeit. 1923, 47, 141–142; J. Soc. Chem. Ind. 1923, 42, 278A).

The copal obtained from South America is collected mainly from the living trees, *Hymenœa Courbaril* (Linn.), but it is also found in the fossil form. It forms the 'Demerara animi' of commerce. For description and solubilities of Demerara, Columbian, and Brazilian copals, *v.* Coffignier (Bull. Soc. chim. [iii.] 35, 1143; 1914, [iv.] 15, 780).

Kauri copal is a fossil resin derived originally from the kauri pine, *Dammara australis* (Lamb.). It is found principally in New Zealand. Tschirch and Niederstadt (Arch. Pharm. 239, 145) found 100 parts of the resin to contain: *kauric acid* $C_{10}H_{16}O_2$, m.p. 192°, 1·5; α- and β-*kaurolic acids*, $C_{12}H_{20}O_2$, m.p. 48°–50°; *kaurinolic acid*, $C_{17}H_{34}O_2$, m.p. 128°–130°, and *kauronolic acid*, $C_{12}H_{21}O_2$, m.p. 86°–89°, 20–22; essential oil, 12·5; *kauroresene*, 12·2; bitter substance, 0·5–1 parts. The solubilities of the commercial

varieties in different solvents are given by Coffignier (Bull. Soc. chim. [iv.] 5, 289).

East African copal, known in commerce as Zanzibar anime or Zanzibar copal, is collected in British, German, and Portuguese East Africa. It is a fossil resin found chiefly in localities from which copal trees have now disappeared, and is derived from *Trachylobium verrucosum*. Examined by Stephan (Arch. Pharm. 234, 552), Zanzibar copal was found to contain two isomeric dibasic hydroxy acids, $C_{56}H_{88}O_8$, *trachylolic acid*, m.p. 165°, and *isotrachylolic acid*, m.p. 105°–107°, the former differing from the latter by being precipitated from alcoholic solution by lead acetate. Two resenes were also found to be present, *α-copalresene*, m.p. 75°–77°, soluble in ether, and *β-copalresene*, insoluble in ether and decomposing at 140° without melting. The resin contains 80 p.c. of trachylolic acid, 4 p.c. of the isomeride and 6 p.c. of the resenes.

West African copals are of very variable quality, the best sorts being fossil or semi-fossil whilst the medium and poorest qualities are procured from living trees. The best West African copals, at the present day, are those from Angola, Benguela, and the Congo. Sierra Leone and Accra copals are of medium quality, and Niger copal is the poorest. Inquiries made during the last few years in the British West African Colonies leave little doubt that Sierra Leone copal is obtained from *Copaifera Guibourtiana* (Benth.), Gold Coast or Accra copal from *Cyanothyrsus Ogea* (Harms.), and Niger copal from *Daniella oblonga* (Oliver) (Imp. Inst. Rep. No. 63, 171). For investigation of Kissel copal, *v.* Coffignier (Bull. Soc. chim. [iii.] 33, 169); Cameroon copal, Coffignier (*l.c.*); Tschirch and Rachwitz (Arch. Pharm. 245, 145); Accra copal, Coffignier (*l.c.*); Kahan (Arch. Pharm. 248, 443); Angola copal, Tschirch and Rackwitz (*l.c.*), Coffignier (Bull. Soc. chim. [iv.] i. 1131); Benin copal, Kahan (Arch. Pharm. 248, 433); Benguela and Congo copals, Coffignier (Bull. Soc. chim. [iv.] i. 1131); Engel (Arch. Pharm. 246, 293); copals from Nigeria and the Gambia (Imp. Inst. Rep. No. 63, 176); Loango copal, Willner (Arch. Pharm. 248, 265); Sierra Leone copal, Coffignier (Bull. Soc. chim. [iv.] i. 1131), Engel (*l.c.*), Willner (Arch. Pharm. 248, 285).

The acid and saponification numbers of several varieties of copals are given by Lippert and Reissiger (Zeitsch. angew. Chem. 1900, 1047); Worstall (J. Amer. Chem. Soc. 25, 860).

Cuapinole Resin is the product of a tree indigenous to a considerable area along the southern portion of the Mexican coast. It consists of small lumps varying in size from that of a pea to a hickory nut, contaminated with foreign matter and some colouring substances which cause the resin to turn very dark when melted. Most of the lumps are nodular, resembling dammar, but others show clear, sharp fractures like Congo copal. The cleanest lumps of the resin have an average acid value of 94·5, with a saponification value of 89–110. A considerable proportion of unsaponifiable matter soluble in ether is present, together with about 60 p.c. of resin acids and also matter insoluble in alcohol and benzol. The material loses about 8 p.c. when heated at 105° for 48 hrs. The resin is not soluble to any extent in organic solvents, but after " running ' at 293° it becomes soluble in both linseed oil and turpentine. When made into varnish with linseed oil, it gives a dark-coloured product, tougher and more elastic but softer than one made with Congo copal (H. A. Gardner and P. C. Holdt, U.S. Paint Manufacturers' Assoc., Circ. 192, Nov. 1923; J. Soc. Chem. Ind. 1924, 43, B 140).

Dammar Resin (*East Indian Dammara Resin*; *Dammar Puti*). The dammar resins are obtained from species of *Hopea*, *Shorea*, and *Balanocarpus*, mainly in the Federated Malay States, Sumatra, and other Dutch East Indian Islands. Small quantities of dammar-like resins are obtained in India, but so far as European commerce is concerned these are of no importance (Imp. Inst. Rep. No. 63, 182). The resin exudes and dries on the trees in lumps of various shapes and sizes, and is collected. It is partially soluble in alcohol, more so in ether, and almost completely in fixed and volatile oils. It is entirely soluble in sulphuric acid. The resin has been examined by Dulk (J. pr. Chem. [i.] 45, 16); Schrötter (Pogg. Ann. 59, 72); Graf (Arch. Pharm. [iii.] 27, 97); Glimmann (*ibid.* 234, 584).

When crude dammar is treated with weak alcohol, a portion, about one-third, dissolves; this is the *α-resin* or hydrated *dammarylic acid* of Dulk. From the residue, absolute alcohol extracts the *β-resin* or anhydrous *dammarylic acid*. By treatment of the residue with ether, according to Dulk, a hydrocarbon *dammaryl* $C_{45}H_{72}$ is dissolved. Dammaryl is a tasteless, inodorous powder which softens at 145° and melts at 190°. When it is exposed to the air it undergoes oxidation until a substance is formed having the composition of the original resin. Graf, however, denies the presence of this hydrocarbon. Glimmann finds the resin to consist of *dammarolic acid*, a dibasic acid $C_{56}H_{80}O_8$, 23 p.c.; *α-dammar-resene* $C_{11}H_{17}O$, m.p. 65°, 40 p.c.; *β-dammar-resene*, m.p. 200°, 22·5 p.c. The β-dammar-resene consists of the portion of the crude resin which is insoluble in absolute alcohol. The ethereal oil obtained by distilling the resin with steam boils at 82°. For description and analytical results of different varieties of dammar, *v.* Imp. Inst. Rep. No. 63, 182; Dieterich (Pharm. Centh. 40, 453); Coffignier (Bull. Soc. chim. 1911, [iv.] 9, 549); Zinke and Unterkreuter (Monatsh. 1918, 39, 865; Chem. Soc. Abst. 1919, i. 166), and for detection of colophony in dammar resin, Hirschsohn (Zeitsch. anal. Chem. 37, 456).

Dragon's Blood Resin. *Resina Draconis* (*Sangdragon*, Fr.; *Drachenblut*, Ger.). The name ' dragon's blood ' has been employed from ancient times to designate various red resinous exudations, but it is chiefly applied now to the crimson-red resin which exudes and dries on the fruits of the rotany or rattan palm, *Calamus draco* (Willdenow), of the East Indies. The drug appears in commerce for the most part in two forms—the one consisting of sticks of resin wrapped in palm leaves, the *reed dragon's blood*; the other, the *lump dragon's blood*, being blocks or irregular-shaped masses (Flück. a. Hanb. 673). Dragon's blood has a sweetish, somewhat acrid taste, and melts at about 120°, when it is said to evolve benzoic acid. It dissolves in alcohol, benzene, chloroform, carbon disulphide, glacial acetic acid, and caustic soda.

In light petroleum it is insoluble, and it dissolves but sparingly in oil of turpentine or ether. It is employed as a colouring agent in pharmacy, and for varnishes.

Among other resins to which the name dragon's blood has been given are: *Socotrine Dragon's Blood*, obtained from trees of the genus *Dracæna* in the island of Socotra (Balfour, Pharm. J. [iii.] 14, 372); *Canary Islands Dragon's Blood*, derived from *Dracæna Draco* (Linn.); and *West Indian Dragon's Blood*, which is produced by *Pterocarpus Draco* (Linn.); and *Croton Draco* (Schlecht) (*v.* Flück. a. Hanb.). According to Dobbie and Henderson (Pharm. J. [iii.] 14, 361), who examined a large number of specimens, the dragon's blood of commerce consists of four distinct products. The *Calamus*, or East Indian resin, agreed with the characters given above, except that it was freely soluble in ether.

The dragon's blood imported in the form of sticks has been examined by Dieterich (Arch. Pharm. 234, 401). It melted at 70°. If the crude resin is extracted with ether, and alcohol added to the extract, *dracoalban* $C_{20}H_{30}O_4$ is precipitated. It is a white amorphous powder which softens at 192°–193° and decomposes above 200°. On evaporation of the solution after removal of the precipitate and extraction of the residue with light petroleum, *dracoresene*, $C_{26}H_{44}O_2$, a bright yellow amorphous resin, m.p. 74°, is obtained. The portion insoluble in light petroleum is a mixture of pure resins of a red colour—the *dracoresinotannol* salts of benzoic and benzoylacetic acids. The red resin consists mainly of dracoresinotannol benzoate. On hydrolysis, dracoresinotannol, $C_8H_9O{\cdot}OH$ is obtained as a bright brown amorphous powder which softens at 100°–105° and then decomposes without melting: 18·4 p.c. of plant remains and 8·3 p.c. of ash were also present.

Blyth and Hofmann (Chem. Soc. Trans. 2, 334) found toluene and styrene among the products of the destructive distillation of dragon's blood (*cf.* Glénard and Boudault, Compt. rend. 17, 503; 19, 505). When fused with potash the resin yields benzoic and *p*-hydroxybenzoic acids and phloroglucinol (Hlasiwetz and Barth, Amalen, 134, 283); distilled with zinc-dust, styrene, toluene, and other products (Bötsch, Monatsh. 1, 609), and by the action of nitric acid, oxalic and nitrobenzoic acids (Blumenau, Annalen, 67, 127).

Eucalyptus Resin. Obtained from the leaves of *Eucalyptus Globulus* (Labill.). It is coloured carmine-red by sulphuric acid (Hartzer, Ber. 9, 314).

Fossil Resins. *Amber, Succinite, Bernstein.* A hard, generally yellow or orange resin thrown up by the sea, along the Baltic coast, especially in Prussia, and in smaller quantities throughout the world (*v.* Rose, Annalen, 28, 339). Amber is tasteless and brittle, and admits of a fine polish. It is much used as an ornament. It becomes negatively electric by friction. The sp.gr. of amber varies from 1·05 to 1·10, and it ranks 2 to 2·5 in the scale of hardness. There can be no doubt that amber is the fossil resin of extinct coniferæ (Göppert, *ibid.* 21, 71). The character of the insects which it includes, and which often render it very beautiful, are an evidence in support of this view.

Amber contains 0·24 to 0·48 p.c. of sulphur (Baudrimont, J. 1864, 538). When heat is applied to it there is evolved, in the first place, succinic acid, water, oil, and combustible gases; the residue is then soluble in alcohol and oil of turpentine. A further application of heat brings over a colourless oil, *oil of amber*, which, when the distillation is well managed, amounts to 28 p.c. of the original resin. Finally, when the temperature rises at the close of the operation, a yellow *wax* condenses. Oil of amber is a mixture of several hydrocarbons. The lighter portion is coloured blue by hydrochloric acid, and decomposed by sulphuric acid, whilst the heavier portion is unacted on by these reagents. Commercial oil of amber is, however, mostly distilled from other, cheaper resins.

Tschirch and Aweng (Arch. Pharm. 232, 660) find that the portion of succinite soluble in alcohol consists principally of *succinoabietic acid* $C_{80}H_{120}O_5$, with a small proportion of the bornyl ester of this acid and some sulphur. The portion (70 p.c.) of succinite insoluble in alcohol is almost entirely composed of the succinate of a resin alcohol *succinoresinol*. Succinoabietic acid is crystalline and melts at 148°, and when fused with potash it yields succinic acid. Succinoresinol is a white amorphous powder soluble in a mixture of alcohol and ether and melting at 275°.

Imitation amber is formed by strongly pressing together waste amber in small pieces; in polarised light it shows brilliant interference colours, whereas genuine amber is homogeneous and doubly refractive. The harder copals, which may also be fossil, sometimes closely resemble amber. They do not scratch rock salt crystals, however, nor do they evolve hydrogen sulphide on heating, which can generally be detected when amber is strongly heated in a narrow test-tube. The formation of succinic acid on dry distillation is further very characteristic for amber.

Amber was formerly much esteemed in medicine; but it is now used chiefly as an ornament, sometimes for photographic and fine varnishes, and in the manufacture of artificial silk.

Ambrite.—The lignite formation in Auckland, New Zealand, furnishes this resin in large lumps. It is brittle, semi-transparent, and of a yellowish-grey colour. Its sp.gr. is 1·034, and its hardness 2. It is insoluble in most solvents, but dissolves partly in carbon disulphide. It contains 0·59 p.c. moisture and 0·18 p.c. ash. The dried ash-free resin contains C 80·95 p.c.; H 9·87 p.c.; O 9·18 p.c. (Bedson, Trans. Fed. Inst. Mining Eng. 16, 338).

Anthracoxene.—This resin is found between the coal strata near Schlau in Bohemia. When seen in masses it is brownish-black in colour, but in thin layers is hyacinth red. It is brittle and swells when heated. According to Laurentz anthracoxene is a mixture of several resins (Sitz. Ber. K. Akad. Wien. 21, 271; J. pr. Chem. [i.] 69, 428).

Asphalt.—This substance, found in various parts of the world, is probably the result of the decomposition of vegetable matter, and is closely allied to petroleum. *V.* Asphalt.

Berengelite, Berengela resin.—A bituminous resinous mineral found in Peru. It is used for caulking ships. It has a dark-brown colour and

is soluble in alcohol or ether, and melts below 100° (Johnston, Phil. Mag. [iii.] 14, 87).

Boloretin.—Derived from the fossil fir wood found in the Danish peat bogs. It is soluble in ether, but not in cold alcohol, and melts at 75° to 79° (Forchhammer, Annalen, 41, 44 ; Krämer, Arch. Pharm. [ii.] 27, 73).

Brusterort Resin, Unripe amber.—This fossil resin resembles krantzite and differs from amber in not containing succinic acid (Spirgatis, J. 1871, 1188 ; 1872, 1146).

Bucaramanga Resin.—Boussingault examined this resin (Ann. Chim. [iii.] 6, 507). It comes from Bucaramanga in New Granada. In appearance it resembles amber, but it does not contain succinic acid.

Burmite.—A semi-transparent resin found near Maingkhwan, in the Hukong valley (Helm, Records Geol. Survey India, 25, 180 ; 21, 6, 9 ; Schriften Ges. Danzig, 8, 63).

Cedarite, Chemawinite.—An amber-like resin found on the shore of Cedar Lake near the mouth of the North Saskatchewan. It occurs as isolated grains rarely as large as a pea and never larger than a walnut (Harrington, Amer. J. Sci. 24, 332 ; Klebs, Jahrb. Min. 1898, ii. 212).

Copalin, Highgate resin.—The blue clay of Highgate Hill contains roundish lumps of this fossil resin. It was studied by Johnston (Phil. Mag. [iii.] 14, 87) and Bastick (Pharm. J. 8, 339). It resembles copal.

Euosmite.—An aromatic resin found in the lignite of Thumsenreuth in Bavaria. It consists of brownish-yellow pulverulent masses or lumps.

Gedanite.—A resin found with succinite on the Baltic coast. It closely resembles succinite but melts at a lower temperature, contains less sulphur and no succinic acid (Helm, Schriften Ges. Danzig, 4, No. 3, 214 ; Arch. Pharm. 233, 191 ; Tschirch and Aweng, *ibid.* 232, 660).

Glessite.—A resin found with gedanite and succinite. It has characteristic spherical microscopic cell-like forms (Helm, Schriften Ges. Danzig, 5, Nos. 1–2, 291 ; Tschirch and Aweng, Arch. Pharm. 232, 660).

Guayaquillite.—From Guayaquil in South America (Johnston, Phil. Mag. [iii.] 13, 329).

Hartin.—A white, inodorous, and tasteless resin found in the lignite of Oberhart, Austria. It is said to have the composition $C_{10}H_{17}O$ (Schrötter, Pogg. Ann. 54, 45).

Hartite.—Another resin found in the same place as hartin. According to Schrötter (*ibid.* 54, 45), it consists of a hydrocarbon of the formula C_3H_5. Hartite has also been investigated by Haidinger (*ibid.* 54, 261), and by Rumpf (J. pr. Chem. [i.] 107, 189).

Ixolite.—Occurs together with hartite (Haidinger, Pogg. Ann. 56, 345).

Jaulingite.—From Jauling in Austria (Ragsby, Sitz. Ber. K. Akad. Wien. 16, 366).

Krantzite.—This is a variety of retinite (Bergemann, J. pr. Chem. [i.] 76, 65).

Middletonite.—The coal seams near Leeds and at Newcastle contain this resin. It was analysed by Johnston (Phil. Mag. [iii.] 12, 261). Two similar fossil resins found in the coal measures were examined by Macadam (Chem. News, 59, 61).

Piauzite.—An earthy resin examined by Haidinger (Pogg. Ann. 42, 275). Hardness 1·5, sp.gr. 1·22, and m.p. 315°.

Pyroretin.—A brown resin from the lignite of Salesl, near Aussig in Bohemia (Stanek, Sitz. Ber. K. Akad. Wien. 12, 551).

Retin Asphalt.—This is a yellow-brown earthy-looking resin, the sp.gr. of which varies from 1·07 to 1·35. That from the lignite of Bovey in Devonshire was examined by Hatchett (Phil. Trans. 1804, 404) and later by Johnston (*ibid.* 1840, 347). Johnston found it to consist of 13·23 p.c. mineral matter, 27·45 p.c. resin insoluble in alcohol and 59·23 p.c. resin soluble in alcohol. The resin soluble in alcohol gave the formula $C_{40}H_{54}O_6$, and was called by Johnston *retinic acid.* Other varieties of retin asphalt occur in the neighbourhood of Halle in Germany (Bucholz, Schw. J. 1, 290) and near Cape Sable in the United States.

Retinite, Walchovite.—This resin, of which there are several varieties, occurs in the coal mines of Walchow in Moravia (Schrötter, Pogg. Ann. 59, 61 ; Cerutti, Arch. Pharm. [ii.] 22, 286). Retinite from Thessaly, *v.* Zengelis (Chem. Zentr. 1901, ii. 833).

Schleretinite.—Obtained from the coal mines of Wigan (Mallet, Phil. Mag. [iv.] 4, 261).

Tasmanite.—The aluminous rocks along the Mersey river in Tasmania yield small scales or plates of this resin. It contains sulphur, and, according to Church (Phil. Mag. [iv.] 28, 465), has the formula $C_{40}H_{62}O_2S$.

Val d' Arno Superiore Resin.—This fossil resin, called by the peasantry 'terra che brucia,' closely resembles the Weissenfels resins. Alcohol separates it into *α-resin* $C_{40}H_{64}O_8$, melting at 75°–90°, and *β-resin* $C_{40}H_{58}O_5$, which melts above 120° (Guareschi, Cimento, 5, 175).

Xyloretin.—A crystalline resin having the formula $C_{10}H_{16}O$ found in the fossil pine trunks of the Danish peat-bogs. It is insoluble in water, soluble in alcohol, and melts at 165°. Heated with potassium it gives a metallic derivative, with liberation of hydrogen (Forchhammer, Annalen, 41, 42 ; Schrötter, Pogg. Ann. 59, 54).

Resins of Weissenfels Lignite.—A series of resinous substances have been isolated from the products of distillation of this lignite. They have been investigated by Brückner (J. pr. Chem. [i.] 57, 1) and Wackenroder (Arch. Pharm. [ii.] 60, 23). For other fossil resins, *v.* Dana Mineralogy, 6th ed., 1002.

Guaiacum Resin. *Guaiaci resina,* B. P. ; *Guiacum,* U.S. P. (*Résine de Gaïac,* Fr. ; *Guaiakharz,* Ger.). Two West Indian species of guaiacum tree, *G. officinale* (Linn.) and *G. sanctum* (Linn.), yield the resin (Flück. a. Hanb. 100 ; Bentl. a. Trim. 41). It is obtained partly as a natural exudation, partly by means of incisions, and in some places the trees are cut down and the trunks set on fire at each end, when the warm resin exudes freely from incisions made in the middle. In commerce guaiacum resin appears in 'tears' or in masses. It is brittle, and, although at first of a reddish colour, becomes greenish by superficial oxidation (*v.* Schiff, Annalen, 111, 372). It has a faint balsamic odour, although it contains no benzoic or cinnamic acid. The sp.gr. is 1·20 and it melts at about 85°, when the balsamic odour is more marked. The resin is soluble in alcohol, ether, acetone, chloroform, and in caustic alkalis ; but in benzene or carbon di-

sulphide it only dissolves partially. Solution of guaiacum resin in alcohol is a very sensitive reagent for oxidising agents. Ferric chloride, for instance, strikes with such a solution a dark-blue colour. Reducing agents discharge the colour, which reappears on oxidation (*v.* Schönbein, Zeitsch. anal. Chem. 8, 67 ; J. pr. Chem. [i.] 102, 164 ; Schaer, Zeitsch. anal. Chem. 9, 430 ; Schönn, *ibid.* 9, 210). According to Kowalewsky (Chem. Zentr. 1889, 210), the action of ozone on the resin gives rise, not simply to a blue-coloured product, but to a series of colours of which blue is about the middle member. This observer notices that the presence of moisture is necessary, ozone giving no colour with dry guaiacum (*v.* Hager, Zeitsch. anal. Chem. 26, 261). The solution is not coloured blue by hydrogen peroxide, a reaction which serves to distinguish that compound from ozone. In presence of such a substance as blood, however, the blue colour appears. If a spot of blood be moistened with freshly prepared alcoholic solution of the inner unoxidised portions of guaiacum resin, and then with an ethereal solution of hydrogen peroxide, a blue colour is produced which can often be made more evident by transference to white blotting paper. This property of guaiacum is occasionally resorted to as a *means of identifying blood stains.* Further investigations have been made on the nature and formation of guaiacum blue by Doebner (Arch. Pharm. 234, 614) ; Schaer (Verh. Natur. Ges. Basel, 13, 287) ; Petit and Mayer (Compt. rend. 141, 193) ; Neumann-Wender (Chem. Zentr. 1905, i. 122) ; Carlson (Zeitsch. physiol. Chem. 55, 260). For methods of testing guaiacum resin, *v.* Hager (Zeitsch. anal. Chem. 26, 261), and for detection of colophony, Hirschsohn (*ibid.* 37, 459).

Crude guaiacum resin heated with an alcoholic solution of caustic potash yields a salt of *guaiaretic acid* $C_{20}H_{26}O_4$ ($C_{20}H_{24}O_4$, Schroeter, Lichtenstadt and Irineu, Ber. 1918, 51, 1587), which falls to the bottom of the vessel in a crystalline form (Unverdorben, Pogg. Ann. 16, 369). The free acid constitutes 10 p.c. of guaiacum resin. It is insoluble in water, but is soluble in alcohol, ether, and most solvents. It melts at 86°. Guaiaretic acid is not coloured blue by oxidising agents. It is optically active, $[\alpha]_D = -94°$ in alcohol, and unsaturated. It yields a diacetyl and a benzoyl derivative (Herzig and Schiff, Ber. 30, 378 ; Monatsh. 18, 714). If the alcoholic mother-liquor from the potassium guaiaretate be treated with hydrochloric acid a heavy amorphous precipitate falls, which, after washing, yields to ether the α-resin or *guaiaconic acid.* This constitutes 70 p.c. of the crude resin. It was isolated by Hadelich (J. pr. Chem. [i.] 87, 321), and also studied by Doebner and Lücker (Arch. Pharm. 234, 590). After treatment of the hydrochloric acid precipitate with ether, there remains a residue amounting to about 10 p.c. of the original resin. This is the *β-resin.* It is soluble in alcohol and acetic acid, but insoluble in ether, benzene, chloroform, and carbon disulphide. Besides a little gum and mineral matter two other constituents have been found in small quantity in guaiacum. One of these is *guaiacic acid* $C_{12}H_{16}O_6$, which occurs only in traces in the resin but in much larger proportion in guaiacum wood (Thierry, J. Pharm. Chim. 27, 381). It forms colourless needles which sublime unchanged and are soluble in water and alcohol. The other substance is a colouring matter *guaiacum yellow*, first noticed by Pelletier and obtained by Hadelich in pale yellow octahedral crystals, $C_{20}H_{20}O_7$, m.p. 115° (D. and L.). It is a weak acid, and dissolves in sulphuric acid with a transient blue colour.

Guaiaconic acid was isolated from guaiacum resin by Richter (Arch. Pharm. 244, 90), who extracted the resin with boiling benzene and precipitated the concentrated extract with light petroleum. The precipitate was then extracted with ether to which chloroform was added as the extraction progressed : this extract was then added to light petroleum which precipitated the guaiaconic acid. This was dissolved in benzene from which solution *β-guaiaconic acid*, $C_{21}H_{26}O_5$, crystallised in small rhombohedra. It melts at 127°, forms a dibenzoyl derivative, m.p. 138°, is insoluble in aqueous alkali hydroxides and is not changed to blue by oxidising agents. The benzene mother-liquor contained *α-guaiaconic acid* $C_{22}H_{26}O_6$, or $C_{22}H_{24}O_6$, which was obtained as a light powder by evaporating the mother-liquor and dissolving the residue in a mixture of ether and chloroform and precipitating by pouring into light petroleum. It melts at 73°, forming a green liquid which becomes brown at 101°, forms a tribenzoyl derivative, m.p. 133°–135°, and is insoluble in aqueous alkalis. Under the influence of oxidising agents, or exposed to the air, α-guaiaconic acid changes to a blue substance $C_{22}H_{24}O_9$; it is the only constituent of the resin which is thus coloured on oxidation.

The products of the destructive distillation of guaiacum are interesting. The lighter portions contain *guaiacene*, *guaiol*, or *tiglic aldehyde* $CH_3{\cdot}CH{:}C(CH_3)COH$ (Deville, Compt. rend. 17, 1143 ; 19, 134 ; Volckel, Annalen, 89, 346). Among the heavier products are guaiacol creosol and pyroguaiacin. *Guaiacol*

$$C_6H_4(OCH_3)OH[1:2]$$

is the monomethyl ether of catechol. *Creosol* $C_6H_3(CH_3)(OCH_3)OH[1:3:4]$ is the monomethyl ether of homocatechol (Hlasiwetz, Annalen, 106, 339). It is a faintly aromatic smelling oil, which boils at 200°, and may be prepared by distilling homovanillic acid with lime (Tiemann and Nagai, Ber. 10, 206). *Pyroguaiacin* condenses towards the close of the distillation in pearly crystals. It was investigated by Pelletier and Deville (Compt. rend. 17, 1143), Ebermayer (J. pr. Chem. [i.] 112, 291), Nachlauer (Annalen, 106, 382) and Hlasiwetz (*ibid.* 106, 381 ; 112, 182). According to Wieser (Monatsh. 1, 595), it has the formula $C_{18}H_{18}O_3$, whilst Herzig and Schiff (*ibid.* 19, 95) give $C_{13}H_{14}O_2$. It is probably 6-hydroxy-7-methoxy-2-3-dimethylnaphthalene. The crystals melt at 180·5°, boil at 258° (80–90 mm.), are nearly insoluble in water and alcohol, and only sparingly soluble in ether. When pyroguaiacin is distilled with zinc-dust it yields the hydrocarbon *guaiene* $C_{12}H_{12}$ in the form of brilliant plates which melt at 97°–98° and possess a faint blue fluorescence. This hydrocarbon is 2-3-dimethylnaphthalene, b.p. 139°–140°/15 mm., m.p. 104°–104·5° (Schroeter, Lichtenstadt and Irineu, *l.c.*). Wieser obtained two other compounds from pyro-

guaiacin: the one by oxidation in acetic acid solution, which gave *guaiene-quinone*, having the formula $C_{12}H_{10}O_2$; and the other by fusion with caustic potash, which yielded a compound m.p. 202°, and has probably the formula $C_{12}H_{12}O_2$. When guaiacum itself is melted with potash, protocatechuic acid is found among the products (Bötsch, Monatsh. 1, 615).

By distilling guaiacum resin under reduced pressure, Richter (Arch. Pharm. 244, 90) obtained tiglic aldehyde, guaiacol, creosol, pyroguaiacin, and a substance which boiled at 255°–260° (4 mm.), resinous in character at first but yielding crystals by the slow evaporation of its solution in benzene and light petroleum. This melts at 107°, has the composition $C_{19}H_{20}O_5$, and forms a dibenzoyl derivative melting at 143°. Guaiaretic acid on distillation yields tiglic aldehyde, guaiacol and pyroguaiacin (Doebner and Lücker); Herzog and Schiff, however, were unable to detect tiglic aldehyde. Guaiaconic acid also yields these three compounds on distillation under ordinary pressure (D. and L.). Under reduced pressure, the acid yielded tiglic aldehyde, guaiacol, and other substances, the formation of which seems to depend on the rate of distillation (Richter).

For the constitution of substances derived from guaiacum resin, *see* Schroeter, Lichtenstadt and Irineu (Ber. 1918, 51, 1587; Chem. Soc. Abst. 1919, i. 84).

Guaiacum is used in medicine as an alterative in gout, rheumatism, and syphilis.

Hemlock Spruce Resin. *Canada Pitch*; *Pix Canadensis* (*Poix de Canada*, Fr.; *Canadisches Pech*, Ger.). The hemlock spruce, *Tsuga canadensis* (Carr.), yields a reddish-brown resin nearly allied to Burgundy pitch, *v.* OLEORESINS.

Indian Hemp Resin (*Cannabin*). The common hemp, *Cannabis sativa* (Linn.), when grown in India develops in the flowering tops of the female plants, a physiological activity not different in kind, but of greatly increased intensity, to that possessed by the plant in Europe or America. For drawings *v.* Bentl. a. Trim. 231. Indian Hemp (*Cannabis Indica*, B. P.; *Cannabis*, U.S. P., is *C. sativa* (Linn.), or the variety *indica* (Lam.). A biological method of assay is given, and alcohol should extract 8 p.c. at least. *Chanvre indien*, Fr.; *Indischer Hanf*, Ger.) contains, together with a *volatile oil*, a *resin* to which the powerful narcotic properties of the drug are due (Roux, J. Pharm. Chim. Feb. 1887). Different varieties of the drug are known in the East as *hashish*, *bhang*, *guaza*, *ganjah*, *charas*. This resin was isolated by T. and H. Smith (Pharm. J. 6, 171) as a brown amorphous solid. The method employed for its extraction was essentially treatment of the dry aqueous extract of the herb with alcohol, purification of the alcoholic solution, and precipitation of the resin therefrom by water.

'Charas,' which consists essentially of the resinous exudation from the stems, leaves, and flower heads of the unfertilised female plant and which is considered by the Indian natives to be the most potent preparation of Indian hemp, has been investigated by Wood, Spivey, and Easterfield (Chem. Soc. Trans. 69, 539). These inquirers have isolated a terpene $C_{10}H_{16}$; a sesquiterpene $C_{15}H_{24}$, identical with the oil isolated by Valenta (Gazz. chim. ital, 10, 540), and afterwards by Vignolo (*ibid.* 25, i. 110) from cannabene, the oil which Personne (J. Pharm. Chim. [iii.] 31, 46) obtained by distilling the hemp plant with water; a paraffin, probably $C_{29}H_{60}$; and a red oil, *cannabinol*, to which the highly characteristic physiological effect of Indian hemp is due. In a further paper (Chem. Soc. Trans. 75, 20), this oil is shown to be a mixture of a compound $C_{21}H_{26}O_2$, for which the name cannabinol is retained, with one or more substances having a lower percentage of carbon. Cannabinol boils at 285° (8 mm.), coming over as an almost colourless oil which on cooling solidifies as a transparent resin. It yields an acetyl derivative, $C_{21}H_{25}O_2{\cdot}CO{\cdot}CH_3$, m.p. 75°. On treatment with cold fuming nitric acid, a trinitro derivative $C_{21}H_{23}(NO_2)_3O_2$ is obtained, crystallising in the form of bright yellow plates, which, when quickly heated, melt at 160° with some decomposition. This compound, on oxidation with hot nitric acid, gives *nitrocannabinolactone* $C_{11}H_{11}NO_4$, identical with the *oxycannabin* of Bolas and Francis (Chem. News, 24, 217) and of Dunstan and Henry (Chem. Soc. Proc. 1898, 44), together with normal butyric, valeric, and other fatty acids. Nitrocannabinolactone crystallises in faintly yellowish needles, melting at 178°. Fränkel (Arch. exp. Path. Pharm. 1903, 49, 266) extracted hashish with light petroleum and distilled the resinous residue (22 p.c.) in a high vacuum. Cannabinol, b.p. 215°/0·5 mm., $C_{21}H_{30}O_2$, contains one hydroxyl group and yields a syrupy acetyl derivative. The other oxygen is aldehydic, *v.* also Czerkis, Annalen, 1907, 351, 467.

Among other constituents occurring in small quantities in Indian hemp, choline (Jahns, Arch. Pharm. 25, 479) and trigonelline have been identified. Possibly the former base is identical with *tetanocannabine* of Hay (Pharm. J. [iii.] 13, 998). The presence of alkaloids has been asserted and denied (Preobraschewsky, Pharm. Zeit. 1876, 705; Siebold and Bradbury, Pharm. J. [iii.] 12, 326; H. F. Smith, *ibid.* [iii.] 22, 267; Warden and Waddell, *ibid.* [iii.] 15, 574).

Jalap Resins. The *true jalap resin* (*Jalapæ resina*, B. P.; *Resina jalapæ*, U.S. P.) is extracted from the tubercles of *Ipomœa Purga* (Hayne) by alcohol, and, after concentration of the alcoholic solution, precipitated therefrom by water. The yield varies from 5 to 18 p.c., usually 8–12 p.c. of the drug employed.

Jalap resin has generally been assumed by investigators to be a mixture of two amorphous glucosidic constituents; one soluble in ether, *jalapin* (about 10 p.c.), and the other insoluble in ether, *convolvulin* (about 90 p.c.). For a record of the work on these substances, *v.* Tschirch (Die Harze, Bd. 11, Leipzig, 1906). Power and Rogerson (J. Amer. Chem. Soc. 32, 80) have shown that jalap resin is much more complex than had been supposed, that its physiologically active components are all indefinite and amorphous, as are also the most important products of their hydrolysis, and that consequently there is no justification for assigning empirical formulæ to these substances. The resin yielded 1·9 p.c. to light petroleum. This extract was physiologically inactive, contained cetyl alcohol and a number of fatty acids; also a *phytosterol* $C_{27}H_{46}O$, m.p. 134°–135°, and a *substance* $C_{18}H_{36}O$, m.p. 56°–57°, which gave the

phytosterol reaction. The ethereal extract amounted to 9·7 p.c. of the resin; it was purgative and containcd a small amount of *ipurganol* $C_{21}H_{32}O_2(OH)_2$, colourless needles, m.p. 222°–225°. It gave the colour reactions of the phytosterols. The chloroformic extract amounted to 24·1 p.c. of the resin and was purgative. It yielded a little β-methyl- aesculetin, and after hydrolysis formic, butyric *d*-α-methylbutyric acids, convolvulinic acid $C_{15}H_{30}O_3$, and possibly a higher homologue of the latter. Some dextrose was also formed so that a portion of the extract was glucosidic. The ethyl acetate extract, which was also purgative, formed 22 p.c. of the resin and on hydrolysis yielded products similar to those of the ethereal extract. The alcoholic extract amounted to 38·8 p.c. of the resin and was purgative It was an almost white powder, m.p. 150°–160°, and gave, on hydrolysis, formic, butyric, and α-methylbutyric acids and also an amorphous product of complex composition. According to U.S. P., when 1 grm. of resin is shaken for 1 hour with 10 c.c. of ether, not more than 12 p.c. should dissolve. For tests of jalap resin, *v.* Cowie (Pharm. J. 1908, 81, 363). Holmes (Pharm. J. 1915, 41, 671) found that Brazilian jalap gave 20 p.c. of resin, answering all B. P. and U.S. P. tests for true or Vera Cruz jalap, and only 0·85 p.c. of the resin was insoluble in ether. The Brazilian variety might compete therefore on favourable terms with that from Mexico.

Besides *Ipomœa Purga* (Hayne), which yields the true jalap resin, there are many other species of the genus *Ipomœa* which possess purgative properties, and a number of these plants, or the resins obtained from them, have been employed in medicine (Power and Rogerson, Amer. J. Pharm. 80, 251; 82, 355; Chem. Soc. Trans. 101, 1). Orizaba Jalap or Mexican Scammony Root of *I. orizabensis* (Ledanois) has been added to the 1914 British Pharmacopœia under the title *Ipomœæ Radix*. It contains 17–18 p.c. of resin, differing from that of true jalap in being readily soluble in ether and in chloroform. Probably it is identical with the ether soluble portion of the resin from *I. purga*. For a complete examination of Mexican Scammony root, *v.* Power and Rogerson (Chem. Soc. Trans. 1912, 101, 1); also for analysis, *v.* Cowie and Brander (Pharm. J. 1908, 81, 366), and Taylor (Amer. J. Pharm. 1901, 81, 105).

Japanese Lacquer (*Urushi*). Urushi is the milky secretion of *Rhus vernicifera* (DC.) and is the material for the well-known Japanesc lacquer varnish.

Ki-urushi (raw lacquer) is collected in June by making shallow cuttings in the stem of the tree when it exudes as drops from between the outer and inner barks. *Seshime-urushi* is an inferior kind of juice which exudes when branches and twigs of the tree have been immersed in water for some months and afterwards heated. The latex, when sent to the market, is usually mixed with more or less 'Mokuyiki,' a substance somewhat resembling urushi. Pure and unaltered urushi is a thick greyish fluid of dextrinous consistence which, under the microscope, is found to consist of minute globules, some of darker, others of lighter colour, mixed with small particles of opaque brownish matter. If the juice be exposed to moist air in a thin layer it dries to a lustrous translucent varnish. According to Yoshida (Chem. Soc. Trans. 1883, 43, 472), it contains urushic acid, gum, water, and a peculiar diastatic matter, also a very small proportion of a volatile poisonous body. The phenomenon of drying is due to the oxidation of urushic acid=urushiol (*see* below) into oxyurushic acid, which takes place by the aid of *laccase* (Bertrand, Ann. Chim. 1898, [vi.] 12, 115; Bull. Soc. chim. 1894, [iii.] 11, 614, 717) in the presence of oxygen and moisture.

Urushiol (=urushic acid of Yoshida, laccol of Bertrand) has been shown by Majima to be catechol with an unsaturated straight side chain of fifteen carbon atoms in a position ortho to one of the hydroxyls, and probably has the formula $(HO)_2{\cdot}C_6H_3{\cdot}C_{15}H_{27}$. It is obtained by distillation in a high vacuum as a viscid brown oil, which is reduced by hydrogen and platinum black to *hydro-urushiol* crystals, m.p. 58°. This substance has been identified with synthetic 1 : 2-dihydroxy-3-pentadecylbenzene (Majima and Chō, Ber. 1907, 40, 4390; Majima, *ibid.* 1909, 42, 1418, 3664; 1912, 45, 2727; Majima and Nakamura, *ibid.* 1913, 46, 4080; 1915, 48, 1597; Majima, *ibid.* 1915, 48, 1593). Urushiol constitutes 60–80 p.c. of the latex, which also contains 20 p.c. of water.

The poison contained in the lacquer is shown by Tschirch and Stevens (Arch. Pharm. 243, 504) not to be volatile but to consist of an oily substance soluble in light petroleum. It produces local dermatitis.

Kamala Resins. Kamala, a fine mobile powder of a dull-red colour, consists of the glands and hairs of the capsules of *Mallotus philippinensis* (Müller, Arg.). The shrub is described by Bentl. a. Trim. 236. Kamala has long been known as an orange dyestuff, and more recently as a remedy for the expulsion of tape worm (Physiological action, *v.* Semper, Arch. exp. Path. Pharm. 1910, 63, 10). Kamala, or a drug closely resembling it, is mentioned as early as the tenth century by the Arabian writers. It grows in Abyssinia, Arabia, the East Indies, and Australia. Good kamala yields at least three-quarters of its weight of resin, but it is often largely contaminated with mineral matter. According to Anderson (N. Ed. P. J. 1, 300; J. 1855, 669), who examined kamala in 1855, it contains: resinous colouring matter, 78·19 p.c.; albuminoids, 7·34 p.c.; cellulose, 7·14 p.c.; water, 3·49 p.c.; and ash, 3·84 p.c. *V.* Kirkby (Pharm. J. [iii.] 14, 897).

Anderson isolated from kamala a crystalline compound *rottlerin*, $C_{33}H_{30}O_9$ (10–12 p.c.), a wax, and a resin melting below 100°; the existence of rottlerin has been confirmed by A. G. and W. H. Perkin (Ber. 19, 3109) and Jawein (*ibid.* 20, 182). A further examination of kamala by A. G. Perkin (Chem. Soc. Trans. 1893, 63, 975; 1895, 67, 230) shows that it contains six distinct substances. Five of these, rottlerin, *iso*rottlerin, a wax, and two resins, one of high and the other of low melting-point, form the principal constituents, but there is also present a small quantity of a yellow crystalline colouring matter. Rottlerin crystallises in thin salmon-coloured plates, m.p. 191°–191·5° (Perkin), 200°–201° (Bartolotti, Gazz. chim. ital. 24, i. 1),

203°–204° (Telle, Arch. Pharm. 1906, 244, 441). It has the molecular formula $C_{33}H_{30}O_9$. It yields a hexa-acetyl derivative and is a derivative of phloroglucinol methylether, like the active substance of *Filix mas* (*q.v.*), which is also used against tape worm. The resin of low melting-point has the composition represented by $C_{12}H_{12}O_3$, and resembles rottlerin, with which it is evidently closely allied in most of its properties. The yellow colouring matter, *homorottlerin*, forms a beautiful glistening mass of yellow needles which melt at 192°–193°. It has the composition $C_{33}H_{36}O_9$ and is possibly a reduction product of rottlerin. The wax is a colourless, apparently crystalline mass, melting at 82°. Iso-*Rottlerin* crystallises in groups of minute plates melting at 198°–199° and in its appearance greatly resembles rottlerin, from which, however, it is readily distinguished by its behaviour towards solvents. The resin of high melting-point is a pale yellow amorphous substance of the formula $C_{13}H_{12}O_4$, closely allied to rottlerin in many of its properties. Kamala also contains a small quantity of a sugar which is extracted from it by water. For substitutes for kamala, *v. Wars* or *Waras resin*.

Kosin Resin (*Koussin*). The female flowers of *Brayera anthelmintica* (Kunth) (*Cusso*, B. P. = U.S. P.) (=*Hagenia abyssinica*, J. F. Gmel), a tree which grows in the higher districts of Abyssinia, contain a crystalline resin, *kosin*. Wittstein (Rep. Pharm. 71, 25) examined koso in 1840, and found the flowers to contain 6 p.c. of an acrid bitter resin, together with wax, gum, and one-fourth of their weight of tannin. Kosin was further studied by Pavesi (J. 1859, 585) and by Bedall (J. 1862, 513). To obtain it the drug is mixed with lime, and extracted first with alcohol and afterwards with water. The solutions are mixed together and concentrated. Acetic acid is then added, which liberates the kosin from its soluble calcium salt, when it slowly precipitates.

Commercial kosin was examined by Flückiger and Buri (J. 1874, 900; Flück. a. Hanb. 258), who found it to consist essentially of yellow rhombic crystals, which melt at 142°. The crystals are insoluble in water, but easily soluble in alcohol, ether, benzene, glacial acetic acid and in alkalis. Ferric chloride gives a red colour with an alcoholic solution of kosin. By repeated crystallisation from alcohol, these crystals have been separated into two compounds, *α-kosin*, melting at 160°, and a little *β-kosin*, more soluble in alcohol and melting at 120°. Both have the composition

$$C_{21}H_{24}O_5(OMe)_2 \text{ or } C_{20}H_{20}O_5(OMe)_2$$

(Boehm and Lobeck, Arch. Pharm. 239, 672; *cf.* Daccomo and Malagnini, L'Orosi, 20, 361). Various other compounds have been obtained from extracts of koso flowers. Leichsenring (Arch. Pharm. 232, 50) isolated *protokosin* $C_{29}H_{38}O_9$, long colourless shining needles, melting at 176°. Protokosin is without physiological action, and the poisonous character of the original drug has been traced to the presence of *kosotoxin* $C_{26}H_{34}O_{10}$, a pale yellow powder (*cf.* Kondakoff and Schatz, Arch. Pharm. 237, 493), which on boiling with baryta is converted into *α*-kosin. Boehm and Lobeck found in a commercial ethereal extract of the flowers a small proportion of *anhydroprotokosin* $C_{58}H_{74}O_{17}$, m.p. 182°. This, when crystallised from alcohol containing a little water, is converted into Leichsenring's protokosin. Also small quantities of *kosidin* $C_{31}H_{46}O_{11}$, melting at 178°, were obtained. The main constituent, however, was kosotoxin, which melted at 62°. When heated with aqueous sodium hydroxide and zinc-dust, kosotoxin is, to a large extent, converted into kosin, and the latter compound is also formed when kosotoxin is boiled with barium hydroxide.

Kosin is employed in medicine as a vermifuge, and it is noteworthy that kosotoxin and *α*-kosin are methylphloroglucinol derivatives, like those of *Filix mas* (*q.v.*), which is also used against tape worms.

Lac Resin. *Gum Lac; Lacca* (*Laque*, Fr.; *Lack*, Ger.). Lac is an exudation produced by the puncture of the hemipterous insect *Coccus lacca* (Kerr), on the young branches of many East Indian lacticiferous trees. The resin exudes and dries on the branch, covering it and imbedding the insects and protecting their eggs. The female insect contains a red colouring matter. The small branches covered with resin are known in commerce as *stick lac*, of which there are under cultivation four crops annually, viz. B. Baisaki (April–July), J. Jetwa (August–October), K. Katkhi (September–November), N. Ncigoli (November–March) (often greatly adulterated). When the resin is removed it is called *seed* or *grain lac*, and when melted by boiling with water and cooled in thin layers it becomes *shellac*, or in round flat pieces, *button lac*. Almost all the shellac of commerce is made in or near Calcutta. It is occasionally mixed with orpiment to improve its colour. The water in which seed or stick lac has been boiled contains the colouring matter, which on evaporation constitutes *lac dye*. Shellac is bleached by treatment with sulphurous acid or chlorine, or by solution in sodium carbonate, and adding sodium hypochlorite solution gradually. The loss of weight on bleaching is about 4 p.c. It gradually deteriorates on exposure to light and air and becomes insoluble in alcohol and alkalis. Unbleached shellac is soluble in alcohol, alkalis, and in hydrochloric and acetic acids. It consists of a mixture of resins, together with small quantities of wax, fat, and extractive matter. The wax varies in amount from 3·6 to 5·5 p.c. It is a mixture of myricyl alcohol, ceryl alcohol, and esters of these alcohols with melissic, cerotic, oleic and palmitic acids. Shellac is used for varnishes, and is the basis of the better kinds of sealing-wax. A liquid shellac is prepared by the action of hot alkalis (Benedikt and Ulzer, Monatsh. 9, 580). *Cf.* Report on Lac and Shellac, by Lindsay and Harlow, Indian Govt. Publication, 1921.

Lac dye was examined by Schmidt (Ber. 20, 1287), who finds it to contain a crystalline compound *lacciac acid* $C_{16}H_{12}O_8$ (?), the salts of which possess the characteristic red colour of the dye. The acid resembles carminic acid. On treating lac dye with boiling benzene a waxy substance, lacceryl lacceroate

$$C_{32}H_{63}O_2 \cdot C_{32}H_{65}$$

is obtained, m.p. 94°, insoluble in alcohol, ether and glacial acetic acid, but soluble in chloroform

and benzene. When saponified with potash it yields an alcohol, *laccerol* $C_{32}H_{66}O$, crystallising from alcohol in lozenge-shaped lamellæ, m.p. 88°, sparingly soluble in cold alcohol, ether, chloroform or benzene. The acid of this ester, *lacceroic acid* $C_{32}H_{64}O_2$, crystallises in lamellæ, m.p. 95°–96° (Gascard, Compt. rend. 1914, 159, 258).

The purified resin of stick lac on hydrolysis yields *aleuritic acid* $C_{13}H_{26}O_4$, m.p. 101·5°, and a sticky substance which is probably a resinotannol (Tschirch and Farner, Arch. Pharm. 237, 35). These investigators also obtained from the colouring matter a substance *erythrolaccin* $C_{15}H_{10}O_5,H_2O$, which appears to be a hydroxymethyl anthraquinone. For the detection and estimation of rosin in shellac, *v.* Langmuir and White (J. Soc. Chem. Ind. 1911, 30, 786; and Allen's Commercial Organic Analysis, 4th ed., vol. iv. 69–74; vol. ix. 311–312). It is best to use the iodine number for this purpose, that of shellac being about 9 and of colophony about 125. Colophony is completely extracted in a Soxhlet from the powdered material mixed with sand, but of the shellac only about 5 p.c. is removed. *Cf.* Hoseason and Klug (J. Soc. Chem. Ind. 1912, 31, 165).

Lanoresin. A resin or gum-resin obtained from the washings of wool (J. Soc. Chem. Ind. 1890, 1046).

Masopin Resin. A resinous substance obtained from the Dschilte tree, and used in Mexico for chewing. It is a snow-white powder, without taste or smell, insoluble in water but soluble in alcohol or ether. From an ethereal solution crystals may be obtained. These melt at 155°, but in melting undergo a change by which the melting-point falls to 70°. Masopin has the composition $C_{22}H_{36}O$ (Genth, Annalen, 46, 124).

Mastic Resin. *Mastiche* (*Mastic*, Fr.; *Mastig*, Ger.). Mastic is the concrete resinous exudation of *Pistacia Lentiscus* (Linn.), an evergreen shrub inhabiting the shores of the Mediterranean (Bentl. a. Trim. 242). It comes chiefly from the island of Scio. Mastic has been known from ancient times, but it is employed less and less in pharmacy, and is being replaced by other resins in the manufacture of the finer varnishes. It occurs in 'tears,' or in masses of a pale-yellow colour; is brittle, and has a faint balsamic odour. It softens in the mouth, and melts at about 108°.

Earlier investigations of the resin have been made by Johnston (Phil. Trans. 1839, 132) and Hartsen (Ber. 9, 316). A sample examined by Tschirch and Reutter (Arch. Pharm. 242, 104) was found to contain α- and *β-masticic acids* $C_{23}H_{36}O_4$, separated from the ethereal solution by 1 p.c. aqueous ammonium carbonate. 1 p.c. aqueous sodium carbonate then extracts *masticolic acid* $C_{23}H_{36}O_4$, crystals, m.p. 201°, and α- and *β-masticonic acids* $C_{32}H_{48}O_4$, melting at 96°–96·5° and 91°–92° respectively. The residue consists of *masticoresenes* with about 2 p.c. of essential oil (*cf.* Flückiger, Arch. Pharm. [iii.] 19, 170). A bitter substance is also present. A table showing the acidity, ether, and saponification numbers of several varieties of mastic is given by Dieterich (Pharm. Centh. 40, 453) and the solubility of the resin in different solvents by Coffignier (Bull. Soc. chim. [iii.] 27, 549).

Maynas Resin (*Calaba, Galba*). A resin extracted by incision from the tree *Calophyllum Calaba* (Jacq.) which inhabits the plains of San Martino and the Orinoco. When purified by solution in alcohol it crystallises in prisms. It is soluble in alcohol, ether, alkalis, and in acetic and sulphuric acids. Analysis led to the formula $C_{14}H_{18}O_4$ (Lewy, Ann. Chim. [iii.] 10, 380).

Mezereon Resin. The acrid constituent of mezereon bark is a resin. The bark is obtained from the shrubs of *Daphne Mezereum* (Linn.) and other species of *Daphne* (*Mezereum*, U.S. P.; *Mezerei Cortex* was deleted from 1914 B. P.). These shrubs, with their red, fragrant flower-clusters preceding the leaves, inhabit southern and middle Europe, and grow in England as far north as Yorkshire (*v.* Bentl. a. Trim. 225–227).

Mezereon *resin* has not been recently examined. It was prepared by Gmelin (Schw. J. 35, 11), and according to Zwenger (Annalen, 115, 17), it yields, on distillation, umbelliferone. Vauquelin (Ann. Chim. 84, 174), also Gmelin and Baer (Schw. J. 35, 1), isolated from various species of daphne a crystallisable compound *daphnin*. This was shown to be a glucoside by Zwenger (Annalen, 115, 1). It breaks up by the action of acids into glucose and *daphnetin* (*q.v.*). Daphnetin has been synthesised by Pechmann (Ber. 17, 929), also Gattermann and Köbner (*ibid.* 32, 287). Among the other constituents of mezereon is a *vesicating fatty oil*, which occurs chiefly in the fruit (Martius, Arch. Pharm. [ii.] 110, 39).

In medicine mezereon is employed as an alterative in rheumatism and scrofula, and is sometimes used as a vesicant.

Norway Spruce Resin. *Burgundy Pitch; Pix Burgundica* (*Poix de Bourgogne*, Fr.; *Fichtentarr* or *Tannenharz*, Ger.). Burgundy pitch is the prepared resin of *Picea excelsa* (Link.), the Norway spruce fir. For drawing *v.* Bentl. and Trim. 261. The market is supplied with Burgundy pitch chiefly from the Grand Duchy of Baden, Austria, and Switzerland. The ordinary method of collection is to make incisions, and to allow the oleoresinous juice which exudes to harden on the trees. It is then removed and treated with boiling water, whereby a resin practically free from volatile oil is obtained. Burgundy pitch closely resembles colophony. It is employed in medicine for plasters. When colophony is melted and mixed with a little fat and water, and stirred as it cools until it solidifies, a mixture is obtained which has the opacity and other characters of Burgundy pitch, and is largely substituted for the true resin.

Palm-Wax Resin. Palm-wax, the product of *Ceroxylon andicolum* (Humb.), a palm of New Granada, contains a resin. It may be separated from the wax by solution in alcohol. It melts above 100°, and is said to have the composition $C_{20}H_{32}O$ (Boussingault, Ann. Chim. [iii.] 29, 330; 59, 19).

Pellitory Resin. The root of *Anacyclus Pyrethrum* (De Cand.), 'pellitory of Spain,' has long been known as a powerful local irritant and sialagogue (*Pyrethri radix*, B. P.; *pyrethrum*, U.S. P.). It comes for the most part from Algeria. A drawing of the plant is given by Bentl. and Trim. 151. The acrid properties of the root seem to depend upon its resinous con-

stituent, *pyrethrin* (Gaultier and Parisol, J. Pharm. Chim. 1818, 49; 1834, 251; Köne, Ann. Chim. [ii.] 59, 328; Thompson, Pharm. J. [iii.] 17, 567). Pellitory contains, besides pyrethrin, fixed oil, gum, inulin, a trace of tannin, and, according to Buchheim (*ibid.* [iii.] 7, 315), a compound *pyrethrine*, analogous to piperine, which, by the action of caustic alkalis, takes up the elements of water and breaks up into *piperidine* and *pyrethric* acid (*cf.* Dunstan and Garnett, Chem. Soc. Trans. 67, 100). Pyrethrine forms white clustered needles, melts at 45° and has an extremely burning taste (Schneegans, Pharm. Zeit. 41, 668).

Similar resinous constituents are found in the root of German pellitory, *A. officinarum* (Hayne) (Bentl. and Trim. 152; Flück. and Hanb. 384).

Pepper Resin. Pepper appears in commerce as 'black,' 'white,' and 'long' pepper. The black and white varieties are the dried fruit of the same plant, the white appearance being due to the removal of the dark-coloured pericarp. Pepper is obtained from *Piper nigrum* (Linn.) (B. P.; *Piper*, U.S. P.), a climbing shrub, indigenous to Travancore and Malabar, and cultivated largely in both the East and West Indies. Long pepper consists of the dried spikes of the minute fruits of *Piper Chaba* (Hunter), a shrub inhabiting the Indian Archipelago (*v.* Bentl. and Trim. 244–245). Pepper has been known from the earliest times. Theophrastus was acquainted with black and long pepper, and white pepper is mentioned by Dioscorides. The Romans levied duty on black pepper in Alexandria, A.D. 176 (Flück. and Hanb. 577).

The pungent taste of pepper is due to its *resin*, but this has not been studied chemically. Pepper contains 2 to 3·8 p.c. of a *volatile oil*, upon which its odour depends. The amount of non-volatile ether extract should be at least 6 p.c. (U.S. P.), and is usually 8–10 p.c. The volatile oil was examined by Dumas (Annalen, 15, 159) and by Soubeiran and Capitaine (*ibid.* 34, 327). It consists essentially of a terpene boiling at 164° to 165°, and having the sp.gr. of 0·873 (Eberhardt, Arch. Pharm. [iii.] 25, 515). The most interesting constituent, however, is the crystalline alkaloid *piperine* $(C_5H_{10}N)C_{12}H_9O_3$, discovered by Oersted in 1819 (Schw. J. 29, 80). It was further investigated by Pelletier (Ann. Chim. [ii.] 16, 344; 51, 199) and others, and Stenhouse found it to be a constituent of cubebs (Annalen, 95, 106). Pepper contains from 5 to 10 p.c. of this compound. By the action of alcoholic potash it breaks up into the base *piperidine* $C_5H_{11}N$, and *piperic acid* $C_{12}H_{10}O_4$. Piperidine may be obtained, as Ladenburg has shown (Ber. 17, 513), by the action of nascent hydrogen on pyridine. An examination of pepper by Johnston (Chem. News, 58, 235; Analyst, 14, 41) has shown that piperidine exists ready formed in the spice to the extent of from 0·2 to 0·8 p.c. Pictet and Court (Ber. 40, 3771), however, by steam distillation of black pepper obtained a distillate which did not contain piperidine, but a base which is probably a C-methylpyrroline, C_5H_9N. According to Buchheim, pepper contains another compound, *chavicin*, which by the action of alkalis yields *chavicic acid* and piperidine (Pharm. J. [iii.] 7, 315).

Pepper is used extensively as a spice. When ground it is liable to adulteration; pepper shells, long pepper, starch, ground olive stones (trade name, poivrette or pepperette), and many other substances have been used. They may be recognised microscopically (*e.g.* Kraemer and Sindall, Amer. J. Pharm. 1908, 80, 1, and chemically, Spaeth, Zeit. Nahr. Genussm. 1905, 1030; Härtel and Will, *ibid.* 1907, 14, 567; Hass and Hoernstein, *ibid.* 1910, 20, 506; Graff. Zeit. offentl. Chem. 1908, 24, 425; Winton, Ogden and Mitchell, Connecticut Exp. Stat. Rep. 1898, 22, 184; and Allen's Commercial Organic Analysis, 4th ed. vii. 54–68) (*v.* PEPPER).

Podophyllum Resin (*Podophylli resina*, B. P.; *Resina Podophylli*, U.S. P.; *Resine de podophylle*, Fr.; *Podophyllumharz*, Ger.). This favourite purgative is obtained from the rhizome and rootlets of May apple, *Podophyllum peltatum* (Linn.), which, with its beautiful wax-like flower, grows abundantly throughout the American continent, east of the Mississippi and south of Hudson's Bay (Bentl. a. Trim. 17). It is also said to occur in Japan (Pharm. J. [iii.] 19, 346). Another species of the genus *Podophyllum*, which yields the Indian podophyllum, *P. Emodi* (Wallich), possesses the same properties as the American species, and is also official (*Podophylli indici resina* and *rhizoma*, B. P.). It inhabits the shady valleys of the Himalayas, and is abundant in Kunawin and Kashmir (Dymock and Hooper, Pharm. J. [iii.] 19, 585). The resin from *P. Emodi* (0·4 grm.) to which 3 c.c. of 60 p.c. alcohol has been added, together with 0·5 c.c. dilute potassium hydroxide, gelatinises on gently shaking; that from *P. peltatum* does not (U.S. P.).

The *resin* is prepared by extracting the dried and powdered drug with alcohol, and throwing the alcoholic solution into water or water acidified with hydrochloric acid, the latter helping the resin to agglomerate, and thus to subside more readily. The precipitate should be dried by simple exposure to the air, or, at all events, at temperatures below 35°. Thus prepared, podophyllum resin has a greyish-white, slightly yellow, or greenish-yellow colour. If higher temperatures be employed the resin is darker. A more distinct yellow colour is produced by the use of alum water as a precipitant. Variations in colour, observable in commercial specimens, have not been found to affect appreciably their physiological activity (Senier and Lowe, Pharm. J. [iii.] 8, 443; Klie, Amer. J. Pharm. 1887, 578; Busch, *ibid.* 1877, 548; Lloyd, Pharm. J. [3] 10, 70; Jones, Chem. Drug. 34, 701). The yield of resin varies from 3 to 5 p.c. From Indian podophyllum 12 p.c. of crude resin was obtained by Dymock and Hooper.

Podophyllum resin is soluble in alcohol and caustic alkalis. From its alkaline solution it is re-precipitated by acids. Although the resin is precipitated from its alcoholic solution by water, it is not insoluble in that menstruum. As much as 80 p.c. may be dissolved in hot water, and only a part of this re-precipitates on cooling. Power finds the crude resin to melt at 120° to 124°. Ether dissolves about 60 p.c. of the resin (*v.* Guareschi, Gazz. chim. ital. 10, 16).

The investigations of Podwyssozki have thrown much light on the chemistry of podo-

phyllum (Arch. Path. u. Pharm. 13, 29 ; Pharm. Zeit. 20, 49, 140, 208, 777 ; Pharm. J. [iii.] 12, 217, 1011). The author reviews experimentally the literature of podophyllum, and isolates a series of definite crystalline and other constituents, the properties of which he has studied, and to one of which he finds the medicinal activity to be due. These compounds exist both in podophyllum and in the resin, but they are more readily obtained from the crude drug. The essential constituent is a colourless, amorphous, poisonous bitter substance, *podophyllotoxin*, which, by the action of lime-water, splits into a neutral, crystalline, bitter, poisonous compound, *picropodophyllin*, and the calcium salt of inactive *picropodophyllic acid*. The colour of podophyllum is due to the compound *podophylloquercetin*, which crystallises in yellow needles with a metallic lustre. The other constituents are inert *podophyllic acid* and an inactive *resin* insoluble in ether. The active purgative constituent is picropodophyllin.

To obtain podophyllotoxin podophyllum is extracted with cold chloroform, which must be free from alcohol, otherwise podophylloquercetin is dissolved also. The chloroform solution concentrated to a syrup is poured into ether, when inert podophyllic acid is precipitated. If the clear liquid is now dropped into light petroleum this solvent retains the fat, and the podophyllotoxin is precipitated as a white powder. It may be purified by re-solution in chloroform and repetition of this process. Thus obtained, podophyllotoxin is a very bitter white or pale-yellow powder, and dissolves in weak spirit or in hot water. It is readily soluble in chloroform or ether, but it is insoluble in light petroleum.

Picropodophyllin is prepared from podophyllotoxin by mixing the alcoholic solution with slaked lime and evaporating to dryness on a water-bath. The residue extracted with hot absolute alcohol yields silky crystals of picropodophyllin on cooling. The resinous compound, picropodophyllic acid, may be prepared from the residue, after extraction of picropodophyllin, in which it exists in combination with calcium. It has no physiological activity, and was not obtained in a sufficiently pure state for analysis. After podophyllum has been treated with chloroform as described, and with light petroleum to remove fat, the podophylloquercetin, which is insoluble in these solvents, is extracted by ether. The ethereal solution is evaporated, and the podophylloquercetin purified by conversion into lead compound, and subsequent regeneration and re-solution in ether. After removal of the ether it remains as a yellow powder, which may be obtained in yellow crystals by sublimation. On exposure to the air it changes to green, a fact which accounts for some of the colours observable in the commercial resin. It has no emetic or aperient action, but is, perhaps, the cause of the intestinal pain which sometimes accompanies the administration of podophyllum. Podophylloquercetin is the colouring agent of podophyllum. It is insoluble in water, and forms with alkalis bright yellow solutions. Ferric chloride colours it dark green.

Kursten (Arch. Pharm. 229, 220), by a slightly modified process, has obtained the constituents discovered by the former chemist in a crystalline condition. He ascribed to podophyllotoxin the formula $C_{23}H_{24}O_9,2H_2O$, and showed that the picropodophyllin obtained from that compound by the action of alkalis is an isomeride, and concluded that the picropodophyllic acid of Podwyssozki is an oxidation product which can be prepared by the action of alkaline potassium permanganate.

Further work by Dunstan and Henry (Chem. Soc. Trans. 73, 209) has proved that the constituents of *P. Emodi* (Wallich) are identical with those of *P. peltatum* (Linn.). Crystalline podophyllotoxin has the formula $C_{15}H_{14}O_6,2H_2O$ and melts at 117°. The anhydrous compound melts at 127°. When acted upon by aqueous alkalis it is converted into the isomeric picropodophyllin which melts at 227°. The acid produced at the same time is not an oxidation product as Kursten supposed but the acid $C_{15}H_{16}O_7$, of which picropodophyllin is the lactone. The yellow colouring matter is concluded to be identical with the quercetin of quercitron bark (*cf.* Kürsten).

The resin *podophyllo-resin* left after the removal of podophyllotoxin and podophylloquercetin from podophyllum resin is a dark coloured powder physiologically active. After purification it is obtained as a transparent reddish-brown substance softening and becoming semi-liquid a few degrees above the ordinary temperature. It yields a crystalline acetyl derivative and probably has the formula $C_{12}H_{12}O_4$. The physiological action of podophyllum is due partly to the podophyllotoxin it contains and partly to the podophyllo-resin. Picropodophyllin, picropodophyllic acid and the quercitrin have very little, if any, purgative action.

The rhizome of *P. Emodi* (Wallich) contains from 10 to 12 p.c. of resin, whereas the American drug contains about 5 p.c. (minimum 3 p.c. U.S. P.).

Various methods for the evaluation of podophyllum resin have been compared by Tanzen (Arch. Pharm. 1916, 254, 44), who prefers that of the Dutch Pharmacopœia, edit. iv. (Apoth. Zeit. 1906, 1072), which stipulates a minimum content of 40 p.c. of podophyllotoxin. 1 grm. of the resin is kept with 10 c.c. of chloroform for 6 hours and shaken frequently. 5 c.c. of the filtrate=0·5 grm. resin is poured into 40 c.c. of petrol, and the precipitated podophyllotoxin is collected after 24 hours, washed with 50 c.c. of petrol and weighed.

Rhubarb Resin (*v.* RHUBARB-ROOT).

Sandarac. *Sandaraca* (*Sandaraque*, Fr. ; *Sandarak*, Ger.). A pale yellow translucent exudate from a small evergreen tree, *Callitris quadrivalvis* (Ventenat), which inhabits north-western Africa. It somewhat resembles mastic, but is brittle between the teeth. It contains three resins which can be separated by means of their different behaviour towards alcohol and alcoholic potash.

Balzer (Arch. Pharm. 234, 289) obtained two resin acids from sandarac, *sandaracolic acid*, m.p. 140°, and *callitrolic acid*, m.p. 248°.

Examined by Henry (Chem. Soc. Trans. 79, 1144), the essential oil of sandarac resin was found to contain a diterpene and *d*-pinene. Two resin acids were isolated, one *i*-pimaric acid

$C_{20}H_{30}O_2$, m.p. 171°, is isomeric with the *d*-pimaric acid isolated by Vesterberg from Bordeaux colophony, but differs from the latter in being optically inactive. The other acid $C_{30}H_{48}O_5$, corresponds to callitrolic acid of Balzer (Arch. Pharm. 234, 289), Tschirch and Wolff (*ibid.* 244, 684), and Balzer have described other acids, which require further investigation.

Australian sandarac or 'white pine resin' is almost entirely the natural exudation product of *Callitris calcarata* (R. Br.) and *C. glauca* (R. Br.) (Smith, J. Soc. Chem. Ind. 30, 1358). It differs from the common sandarac chiefly in the larger size of its 'tears,' the name given to the small hard masses of resin formed on the trees by the evaporation of a portion of the volatile matter. Henry (*l.c.*) found this resin to contain *d*-pinene and the two resin acids already obtained from common sandarac. Sandarac, which is also known in commerce as 'gum juniper,' is used in the preparation of varnishes and as a pill-coating.

Analytical constants of sandarac resin are given by Dieterich (Pharm. Centh. 40, 453) and its solubility in various solvents by Coffignier (Bull. Soc. chim. [iii.] 27, 549).

Scammony Resin. *See* under GUM RESINS.

Tonquin Lac Tree. The sap of the Tonquin lac tree, *Rhus succedanea* (Linn.), which forms the basis of various kinds of lacquer, is a thick, nearly white alkaline cream, superficially oxidisable by air to an intensely black impervious substance insoluble in the usual solvents. Complete oxidation only takes place in the presence of a diastatic ferment *laccase*, which can be separated from the other essential constituents of the sap by means of alcohol, in which it is insoluble. From the portion of the sap soluble in alcohol, a substance *laccol* can be precipitated by lead acetate. It is a thick oil, intensely irritating to the skin. It is readily oxidisable in the air to a reddish, viscous or resinous substance (Bertrand, Bull. Soc. chim. [iii.] 11, 717; Compt. rend. 120, 226). *See* also Japanese Lacquer, in this article, above.

Wars or **Waras Resin.** This drug, which, coming from India or Arabia, has from time to time appeared as a substitute for kamala, consists of the glands and hairs of species of *Flemingia*. The powder resembles kamala, but is of a darker colour. It yields resin to the same extent as kamala, and is closely related to that drug in all its characters. *V.* Flückiger (Pharm. J. [ii.] 9, 279; [iii.] 17, 1029; 18, 110), Kirkby (*ibid.* [3] 14, 897), Dyer (*ibid.* [iii.] 14, 917, 969) and Hooper (*ibid.* [iii.] 18, 213).

An investigation of waras by A. G. Perkin indicates that it contains five distinct substances, *flemingin*, *homoflemingen*, *resins of high and low melting-points*, and a *wax*. There is a close analogy between these compounds and the similar products obtained from kamala. Flemingin $C_{12}H_{12}O_3$, is a dull orange-red, crystalline powder melting at 171°–172°. Homoflemingin consists of pale yellow needles melting at 165°–166°. It has the same composition as flemingin (Chem. Soc. Trans. 73, 660).

Estimation of Resins.—For a comparison of methods for determining resins, *see* R. Jungkunz (Chem. Zentr. 1922, 93, ii. 329–330; J. Soc. Chem. Ind. 1923, 42, 235 A). The method of Fahrion (J. Soc. Chem. Ind. 1911, 1266) gave unsatisfactory results. That of Wolff and Scholze (J. Soc. Chem. Ind. 1914, 363) gives results consistently 2 p.c. too low, while McNicoll's method (J. Soc. Chem. Ind. 1921, 124 T) gives results consistently about 2·5 p.c. too high. McNicoll's method is the best for rapid and approximate determinations of resin acids in mixtures, but where accuracy is required the mean of two determinations by this method and that of Wolff and Scholze respectively should be taken.

Export of Resins, 1921, 1922.—Copal, dragon's blood, gamboge, which is a gum-resin (*v.* GAMBOGE, and GUM RESINS), gurjun-balsam, elemi, and resin are the principal resins produced in Eastern Asia. In 1920, 1,019,834 kgs. of copal were exported to India, Great Britain, United States, Belgium, France, Spain, Japan, China, and Australia, and in 1921 the total shipments were 542,700 kgs. Large quantities of dragon's blood (obtained from *Calamus draco*, which grows in the Dutch East Indies, Straits Settlements, and the Federated Malay States) are shipped to India, China, and Europe from Singapore and Batavia, the two chief export centres. Several trees produce gamboge, the chief variety coming from *Garcinia morella*, which flourishes in Siam, the islands on the east coast of the Gulf of Siam, various parts of India, and the southern areas of Cochin China. The chief export centres are Bangkok, Saigon, and Singapore. Gurjun-balsam, which is exported chiefly from Singapore, is an oleo-resin obtained from several species of *Dipterocarpus*, of which *D. turbinatus* is found in the Straits Settlements and French Indo-China, and *D. trinervis* in Java and the Philippines. The trade in gurjun is mostly carried on between various Eastern countries, and some is also shipped to America and Europe. Kwang-tung and Kwangsi, provinces of China, are the chief sources of supply of resin in Eastern Asia, shipments being exported from Kowloon, Canton, Swatow, and Wuchow. Hongkong imports practically all the Chinese output of resin, Japan being the next largest purchaser. Elemi is produced in the Philippines, Great Britain and the United States being the largest importers (Ch. Comm. J. Oct. 5, 1923; J. Soc. Chem. Ind. 1923, 42, 1230). G. B.

RESIN OIL. *Resin spirit.* Common resin or colophony is a substance which is left in the stills after distillation of spirits of turpentine (*v.* RESINS). It is a well-known brittle, but fusible and inflammable, solid which is found in commerce of various colours, from pale yellow to black. It consists of a mixture of acids, the exact composition of which, notwithstanding numerous researches, remains unknown. It is, however, usually regarded as consisting chiefly of abietic acid. These acids form greasy salts with alkalis, and resin is commonly employed as an ingredient in soap, as well as in the manufacture of varnishes.

The lower grades of resin are submitted to distillation with the object of producing an oil suitable for use as a lubricant, and a spirit which is used in varnish-making. The distillation is carried out in cast-iron stills of charging capacity varying between 3 and 10 tons, the usual size being about 5 tons. The head of the still is rounded and provided with flanges

by which it can be bolted on to the body, which has a hemispherical bottom. The condensing worm is usually made of copper. A considerable quantity of gas is given off during the distillation, containing carbon monoxide and hydrocarbons. The most volatile portion of the distillate, boiling between 80° and 250°, constitutes resin spirit or essence of resin, and is followed by the oil, which distils only between 300° and 400°. The residue in the still is pitch or coke, according to the extent to which the heating is carried. From 1 ton of resin the yield amounts to ½ to 1 cwt. of spirit, and 17 cwts. of oil. Water containing a little acetic acid comes over throughout the distillation, and the crude oils have a milky appearance in consequence.

Resin *spirit* is chiefly used in varnish-making, and as an adulterant of spirit of turpentine. It is refined by agitation with caustic soda and redistillation, or by redistillation only. Crude resin *oil* is a strongly fluorescent viscid oil, about one-fourth of which dissolves in solution of soda, the insoluble part consisting of a hydrocarbon (above 360°). Resin oil has also the property of uniting with slaked lime to form a greasy mass which is used as a lubricant. It is employed chiefly in collieries, and appears to be suitable only for iron bearings. In order to prepare the grease a smooth cream of slaked lime and water is first prepared, and a small portion of the oil is mixed with this in the proportion of about 4 parts of oil to 3 parts slaked lime. The two soon unite, forming a greasy semi-solid mass, with which an additional quantity of oil is afterwards incorporated until the requisite consistence is obtained. The finished grease contains about 1 part of lime to 20–25 parts of oil. The fluorescent bloom of the crude oil can be removed by washing it first with soda lye, and then exposing it to air in shallow iron vessels (Kelbe's patent, Ber. 13, 215a). It is also stated that the bloom can be destroyed by treatment with dinitronaphthalene, with nitrobenzene, or with hydrogen peroxide. Purified resin oil is used to adulterate lubricating oils, and is also mixed sometimes with rape oil and with boiled linseed oil, and forms an ingredient in some printing inks. The resin oils are generally sold under the name 'pine oil' (*q.v.*), and are classified, according to quality, as soft, medium, and hard.

The composition of both the essence and the oil has been studied by many chemists. The former consists of a complex mixture of hydrocarbons and other volatile substances, of which, when distilled, resin spirit generally yields more than half its volume below 120°. The following constituents have been isolated: A pentine, C_5H_8 (b.p. 50°) (Couërbe, J. pr. Chem. 1839, 18, 165); *iso*butyl-aldehyde (Tilden, Ber. 13, 1604); *iso*butyric, caproic and other fatty acids, methyl alcohol (very small quantity, 50 grms. from 150 kilos.); a hydrocarbon, C_9H_{12} (b.p. about 160°), homologue of benzene; ordinary cymene and a new cymene (*m*-propyltoluene); *m-iso*butyl-toluene (b.p. 186°–188°); *p*-butyl-toluene (b.p. 176°–178°) (Kelbe, Ber. 13, 888, 1157; Annalen, 210, 1; Ber. 14, 1240; *ibid.* 15, 308); dipentine, $C_{10}H_{16}$ (Tilden, *ibid.* 13, 1604) together with a relatively large proportion of a heptine, C_7H_{12} (103°–104°), which has been shown by Morris (Chem. Soc. Trans. 1882, 167) to be probably methyl-propyl-allene $CH_3{\cdot}CH : C : CH{\cdot}C_3H_7$. This liquid is characterised by giving a succession of colours (yellow, red, green, and deep blue) when agitated with strong sulphuric or hydrochloric acid. In the presence of air and water it forms a glycol, $C_7H_{12}(OH)_2$, which crystallises with one molecule of water in the form of long slender prisms, which are frequently to be seen in old samples of resin spirit.

Resin oil consists of a mixture of abietic acid $C_{20}H_{30}O_2$ (Levy; Koritschoner; Fahrion; Vesterberg; Tschirch and Wolff, Arch. Pharm. 1907, 245, 1; Ruzicka and Meyer, Helv. Chim. Acta. 1922, 5, 315), *v.* ABIETIC ACID, and small quantities of phenols with a mixture of hydrocarbons $(C_{10}H_{16})_n$ (b.p. above 360°), including *abietene* ($C_{18}H_{28}$, b.p. about 250°) and *colophene*, which constitutes about three-fourths of the whole. W. A. T.

RESOFLAVINE. This yellow dyestuff $C_{14}H_6O_7$, obtained by the action of potassium persulphate and sulphuric acid on 3 : 5-dihydroxybenzoic acid, was first examined by Herzig and Tscherne (Monatsh. 1904, 25, 603). This yields the *acetyl* derivative $C_{14}H_3O_7(C_2H_3O)_3$, and when methylated by means of diazomethane the yellow *trimethyl ether* $C_{14}H_3O_4(OMe)_3$, m.p. 286°–288°.

When heated with methylic iodide and alcoholic potassium hydroxide, resoflavine trimethyl ether is converted into the ester

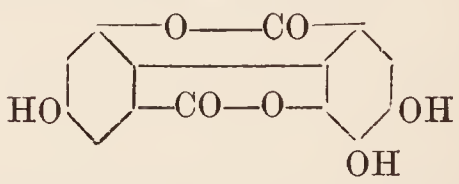
$$COOMe{\cdot}C_{12}H_3(OMe)_5{\cdot}COOMe$$

m.p. 132°–134° (Annalen, 1907, 351, 24); this on hydrolysis gives first the ether acid, m.p. 197°–199°, $COOH{\cdot}C_{12}H_3(OMe)_5{\cdot}COOMe$, and subsequently the dicarboxylic acid

$$COOH{\cdot}C_{12}H_3(OMe)_5{\cdot}COOH$$

which melts at 247°–249°.

By fusion with alkali (Herzig and Epstein, *ibid.* 661) resoflavine gives 3 : 5-dihydroxybenzoic acid, whereas on distillation with zinc-dust fluorene is produced. Resoflavine (Herzig and Tscherne, *ibid.* 1908, 29, 281) is evidently a trihydroxydiphenyldimethylolid—



closely related to ellagic acid, which is in fact to be regarded as its monohydroxy derivative. A. G. P.

RESOPHTHALIN. *Fluorescein v.* TRIPHENYL METHANE COLOURING MATTERS.

RESORCIN BLUE *v.* OXAZINE COLOURING MATTERS.

RESORCIN BROWN. The sodium salt of xylidin-azo-sulphanilic-azo-resorcin. A brown powder, soluble in water and sulphuric acid, forming a brown solution. Dyes wool brown in an acid bath.

RESORCIN YELLOW *v.* AZO- COLOURING MATTERS.

RESORCINOFORM is an amorphous currant red powder prepared by dissolving 110 grms. of resorcinol in about 100 grms. of formaldehyde solution. Sufficient hydrochloric acid is then

added to cause precipitation, the mixture, which turns pink, being kept well stirred. It is then drained on a filter and dried at 25°. Resorcinoform is said to be an active antiseptic for medicinal use (Monteuil, J. Soc. Chem. Ind. 1909, 542).

RESORCINOL. *Resorcin,* 1 : 3-*dihydroxybenzene v.* PHENOL AND ITS HOMOLOGUES.

A brown colouring matter is obtained by adding a cold solution of 3·5 grms. of sodium nitrite in 3·5 grms. of water to a cold solution of 11 grms. of resorcinol in 22 grms. of water, allowing the mixture to remain at room temperature for 2 hours, afterwards raising the temperature to 40°–50°C. during 2–3 hours, and finally concentrating the product to a 25 p.c. paste. The colouring matter yields a green iron lake, indicating that it contains a nitroso group, and it dyes wool a pleasing orange-brown shade. It is suitable for printing wool and cotton fabrics, a satisfactory printing paste consisting of 10 grms. of colour paste, 10 grms. of water, 65 grms. of thickening mucilage, 5 grms. of 40 p.c. acetic acid, and 10 grms. of chromium acetate of 20°B. (sp.gr. 1·16), or 10 grms. of colour paste, 1·5 grms. of borax, 15·5 grms. of water, 66 grms. of thickening mucilage, 3 grms. of sodium bichromate, and 4 grms. of lizarol. This brown colouring matter also readily couples with diazo-compounds such as diazotised *m*- and *p*-nitraniline, yielding similar useful brown to yellowish-brown dyestuffs. When a mixture containing 2 parts of 80 p.c. sulphuric acid, 2 parts of formic acid, and 1 part of resorcinol is maintained at ordinary temperature for several days, an orange-red dyestuff (probably dihydroxyxanthene) is formed which shows a green fluorescence in alkaline solution and yields, on wool, shades fast to washing. When the reaction is allowed to continue for several weeks, an orange-yellow product is obtained which dyes cotton mordanted with tannic acid and antimony.

A similar dyestuff, which is probably an acridine derivative, is obtained by this reaction when the resorcinol is replaced by a mixture containing 1 mol. of *m*-toluylenediamine and 1 mol. of resorcinol, but not when the *m*-toluylenediamine is replaced by pyrogallol or dimethyl-*m*-aminophenol. A brown dyestuff for wool is obtained by oxidation of resorcinol by means of manganese dioxide and an alkali. Orange to yellow dyestuffs having good affinity for wool and but little affinity for mordanted fabric are obtained when 1 mol. of resorcinol is coupled with 1 or 2 mols. of diazotised *m*- or *p*-nitraniline. They resemble alizarin yellow R and G in fastness to washing and are suitable for printing, a satisfactory printing paste consisting of 10·9 of colour-paste (20–25 p.c.), 10 grms. of water, 67 grms. of thickening mucilage, 3 grms. of 40 p.c. acetic acid, and 10 grms. of chromium acetate of 25°B. (sp.gr. 1·21). The dyestuff obtained when 1 mol. of pyrogallol is coupled in acid solution with 1 mol. of diazotised *p*-nitraniline dyes mordanted fabrics but not unmordanted wool, and when printed on cotton mordanted with chromium, it yields a pleasing bistre shade fast to washing. Brown dyestuffs obtained by coupling 1 mol. of toluylenediamine with 1 mol. of resorcinol or 1 mol. of diazotised *p*-aminosalicylic acid with 1 mol. of toluylenediamine are not suitable for printing or dyeing. A pleasing orange-brown dyestuff which is very fast to washing is obtained when diazotised *p*-aminosalicylic acid is coupled with resorcinol. A blue oxazine dyestuff is produced by oxidation of a mixture containing 1 mol. of *p*-aminosalicylic acid and 1 mol. of resorcinol. Meininger reports that the reaction between resorcinol and a concentrated solution of sodium nitrite is not quantitative, and that the dyestuffs produced from pyrogallol are related to the azochromine and azogalleine dyestuffs (E. Lang, Bull. Soc. Ind. Mulhouse, 1923, 89, 24 ; J. Soc. Chem. Ind. May 11th, 1923, 394 A).

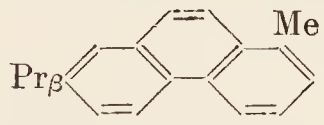
RESORCINOLBENZEÏN *v.* AURIN.

α- AND *β*- **RESORCYLIC ACIDS** *v.* PROTOCATECHUIC ACID.

RESORUFIN *v.* OXAZINE COLOURING MATTERS.

RETAMINE $C_{15}H_{26}ON_2$, from *Retama sphærocarpa* (0·4 p.c. of fresh plant) crystallises from petroleum in needles, m.p. 162°, and is readily soluble in water, ether and chloroform. It is a strong di-acid base, bitter, but otherwise physiologically inert, and apparently allied to sparteine but not identical with the known oxysparteine (Battandier and Malosse, Compt. rend. 1897, 125, 360).

RETENE or 1-Methyl-7-*iso*Propylphenanthrene $C_{18}H_{18}$ (Bucher, J. Amer. Chem. Soc. 1910, 32, 374 ; Lux, Monatsh. 1908, 29, 763 ; *ibid.* 1910, 31, 939 ; Ber. 1910, 43, 688)



(Virtanen, Annalen, 1921, 424, 150), occurs in high-boiling tar oils derived from resinous pine-wood, and forms a faintly yellow, glittering, crystalline powder, which melts to a yellow oil at 98·5°, b.p. 394°. It can be melted together with different oils, fats, and hydrocarbons, and raises or lowers their melting-point accordingly. It can also be obtained by distilling resin oil, abietene abietic acid $C_{20}H_{30}O_2$, dihydroabietic acid, or abietinol with sulphur. Retene reacts with sulphur, yielding a compound, m.p. 86° (Easterfield and Bagley, Chem. Soc. Trans. 1904, 1247). When heated with hydrogen in the presence of nickel oxide, the dodecahydroretene $C_{18}H_{30}$, b.p. 336°, is first obtained, then the perhydroretene $C_{18}H_{32}$, b.p. 300°–315°, which is not identical with fichtellite as had been formerly supposed (Ipatieff, Ber. 1909, 42, 2092 ; Liebermann and Spiegel, *ibid.* 1889, 22, 779).

Bromo- derivatives of retene and of retene quinone, m.p. 197°, have been obtained (Scheller and Heiduschka, Arch. Pharm. 1910, 248, 89).

The fossil resin of the coniferæ, as found in Switzerland, Bavaria, and Denmark, contains retene as its principal constituent. It appears, indeed, very probable that the hydrocarbon is in every case derived from the coniferæ ; *v.* Ekstrand, Annalen, 1877, 185, 75 ; E. v. Boyen, J. Soc. Chem. Ind. 1888, 116.

Further literature on retene and its derivatives : Kelbe, Chem. Zentr. 1887, 1504 ; Ekstrand, Bull. Soc. chim. [ii.] 24, 55 ; Bamberger and Hooker, Ber. 1886, 18, 1024, 1750 ; Schweitzer, Annalen, 1891, 264, 193 ; Perrier,

Compt. rend. 116, 1298; Valeur, *ibid.* 1898, 126, 1148; Wiedemann, Ann. Physik. 1895, [ii.] 56, 18; Bamberger and Grob, Ber. 1901, 34, 533; D. R. P. 151981; Hofmann, Metzler and Lecher, Ber. 1910, 43, 181; Heiduschka and Grimm, Arch. Pharm. 1912, 250, 33; Heiduschka and Khudadad, *ibid.* 1913, 251, 682; Ruzicka and Meyer, Helv. Chem. Acta, 1922, 5, 581.

RETIN ASPHALT *v.* RESINS.

RETINIC ACID *v.* RESINS.

RETINITE *v.* RESINS.

REXITE. An explosive consisting of nitroglycerin, 6·5–8·5 parts; ammonium nitrate, 64–68 parts; sodium nitrate, 13–16 parts; trinitrotoluene, 6·5–8·5 parts; dry wood meal, 3–5 parts.

REXOTAN *v.* SYNTHETIC DRUGS.

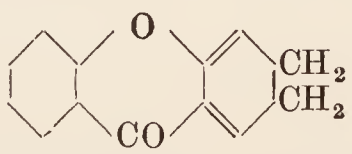
RHABDOPHANE. Hydrated phosphate of cerium and yttrium metals, $RPO_4 \cdot H_2O$. It forms small mamillated or botryoidal groups with a rich brown colour, a certain degree of translucency, and a greasy lustre, much resembling botryoidal zinc-blende in appearance. It has an internal radially fibrous structure; sp.gr. 4·0; H.=3½; soluble in hydrochloric acid. It is a rare mineral from an unknown Cornish locality, and specimens are occasionally found in old collections labelled as blende. The same mineral has been described under the name *scovillite* from the Scoville ore bed at Salisbury, Connecticut, where it occurs sparingly as pinkish or yellowish encrustations on limonite and pyrolusite. L. J. S.

RHAMNETIN *v.* PERSIAN-BERRIES.

RHAMNINOSE *v.* CARBOHYDRATES.

RHAMNOSE *v.* CARBOHYDRATES.

RHAMNUS CATHARTICUS. The *Rhamnus catharticus* or Purging Buckthorn, indigenous to Great Britain, is a stiff many-branched shrub growing from five to ten feet high, the fruit of which consists of small berries, resembling when dry black peppercorns. Formerly it was in great demand as a medicine, but has now fallen into disrepute. The juice of the berries admixed with lime and evaporated to dryness constitutes the pigment known as 'sap' or 'bladder green.' According to Tschirch and Polacco (Arch. Pharm. 1900, 238, 459) the yellow tinctorial constituents yielded by the berries of this plant are quite distinct from those given by the berries of the various species of *Rhamnus* which constitute the Persian berry proper. Thus in addition to rhamno-emodin they isolated four yellow crystalline substances, *rhamnocitrin*, *β-rhamnocitrin*, *rhamnochrysin*, and *rhamnolutin*. Rhamnocitrin was considered to consist of the trihydroxy derivative of a dihydroxanthone—



rhamnolutin of a tetrahydroxyflavone isomeric with luteolin and fisetin, and rhamnochrysin an oxidation product of rhamnocitrin, whereas β-rhamnocitrin was distinct from rhamnetin and indeed contains no methoxy groups.

Waliaschko and Krasowski (J. Russ. Phys. Chem. Soc. 1908, 40, 1502) and Krasowski (*ibid.* 1510) criticised this paper of Tschirch and Polacco, and could not isolate the compounds described by these latter authors. On the other hand, quercetin, rhamnetin, and xanthorhamnin, the glucoside of rhamnetin, were found to exist in these berries, and it seemed likely that the rhamnolutin of Tschirch and Polacco was rhamnetin and their rhamnochrysin a mixture of quercetin and emodin.

Oesch and Perkin (Chem. Soc. Trans. 1914, 105, 2350) also isolated *rhamnetin* from these berries, together with a small amount of quercetin, and considered that the former represents the β-rhamnocitrin of Tschirch and Polacco. The main colouring matter present, however, is *kaempferol*, $C_{15}H_{10}O_6$, the trihydroxyflavonol which can be obtained from the flowers of the *Delphinium zalil* and *D. consolida*, and this is to be regarded as the so-called 'rhamnolutin.'

A fourth compound, evidently the rhamnocitrin of these latter authors, possessed the formula $C_{16}H_{12}O_6$, rather than $C_{15}H_{10}O_5$ which they assigned to it. This crystallised in yellow leaflets, m.p. 221°–222°, and its acetyl derivative at 200°–201°, and these melting-points are practically the same as those given by Tschirch and Polacco. It contains one methoxy group, by the action of hydriodic acid yields *kaempferol*, and is evidently a *kaempferol monomethyl ether*. It bears considerable resemblance to kaempferide a monomethyl ether of kaempferol present in Galanga root, *Alpinia officinarum* (Jahresber. 1881, 14, 2385), which, however, melts at 227°–229°, and its acetyl derivative at 193°–195°. A. G. P.

RHAMNUS FRANGULA. The bark of the alder buckthorn, *R. frangula* (Linn.), a shrub widely distributed throughout Europe, is employed in medicine chiefly in the form of a fluid extract as a mild purgative. Since the beginning of the last century the bark of this plant has been submitted to repeated examination. Casselmann (Annalen, 1857, 104, 77) was the first to analyse its main crystalline constituent which he termed *frangulin*, and this he extracted from the bark by means of ammonia. Faust (Annalen, 1872, 165, 229) by the hydrolysis of frangulin with hydrochloric acid obtained, in addition to a sugar, a substance he termed *frangulic acid*, and as by the distillation of this compound with zinc-dust anthracene was produced he concluded it to be a dihydroxyanthraquinone isomeric with alizarin.

Liebermann and Waldstein did not prepare frangulin (Ber. 1876, 1775) but studied the colouring matter obtained from the bark by means of caustic soda solution, evidently the same substance as Faust's frangulic acid. This they isolated by sublimation and found to consist of emodin, and suggested that the hydrolysis of frangulin with acids might probably be represented by the following equation :—

$$C_{21}H_{20}O_{10}+H_2O=C_{15}H_{10}O_5+C_6H_{12}O_6$$

Faust (Pharm. Zeitschrift für Russland, 17, 257), on the other hand, considered that Liebermann and Waldstein's compound was not in reality emodin but rather a trihydroxydimethyl or a trihydroxyethyl-anthraquinone.

The subject was next studied by Schwabe (Arch. Pharm. 1888, 26, 259), who devoted

special attention to frangulin. To this he assigned the formula $C_{21}H_{20}O_9$, and obtained from it by hydrolysis emodin and a sugar. This latter, which he did not isolate in a pure condition, he regarded as the rhamnodulcite of Liebermann. Finally Thorpe and Robinson (Chem. Soc. Trans. 1890, 57, 38) and Thorpe and Miller (*ibid.* 1892, 61, 1) submitted frangulin to detailed examination, and showed that, as Schwabe had stated, its correct formula is $C_{21}H_{20}O_9$. When hydrolysed it yields emodin, and rhamnose, which was isolated in a crystalline condition, and as a result the reaction may be thus expressed :—

$$C_{21}H_{20}O_9+H_2O=C_{15}H_{10}O_5+C_6H_{12}O_5$$

For the preparation of frangulin the crushed bark is first treated with ligroin to remove wax and chlorophyll and subsequently extracted with alcohol. The extract is evaporated to dryness with sand, the powdered product extracted with ether, and after distilling off the ether the residue is treated with a little alcohol. On standing the solution deposits a mixture of emodin and frangulin together with a small quantity of a more sparingly soluble substance, and these can be separated by fractional crystallisation from alcohol.

Frangulin is an orange-yellow crystalline powder sparingly soluble in alcohol and melts at about 225°. It is readily susceptible to hydrolysis, and this indeed occurs to a slight extent by mere boiling with alcohol.

The sparingly soluble substance which contaminates the crude frangulin, the presence of which was also observed by Schwabe, crystallises from alcohol in golden-yellow needles, melting at 202°–203°. It dissolves in sulphuric acid with a red coloration, in dilute alkalis with the same tint, and is almost insoluble in ammonia. It appears to possess the formula $C_{15}H_{10}O_5$, being thus isomeric with emodin, though Perkin (Chem. Soc. Trans. 1895, 67, 1084) has suggested its possible identity with the emodin methyl ether $C_{16}H_{12}O_5$ of the *Ventilago madraspatana* and *Polygonum cuspidatum*, with which in melting-point and properties it closely agrees. A. G. P.

RHATANY ROOT. The dried root of *Krameria triandra* (Ruiz et Pav.), Peruvian rhatany, or *K. tomentosa* (St. Hill.), Savanilla rhatany. The bark contains about 20 p.c. of a kind of tannin. Is a strong astringent. Other species of *Krameria* produce Para rhatany and Texas rhatany, which are substituted for the first two kinds. For rhatany red *v.* Grabowski, Annalen, 143, 274.

RHEADINE $C_{21}H_{21}O_6N$. Colourless needles, m.p. 245°–247° (Pavesi). Occurs in red poppy, also in opium poppy, opium, and *P. hybridum* (Linn.). Not poisonous. On treatment with acids it is converted into *rheagenine*, m.p. 235° (Hesse, *ibid.* 1866, 140, 146 ; Pavesi, Chem. Soc. Abstr. 1906, 90, [ii.] 483). *Papaver dubium* (Linn.), according to Pavesi (Chem. Soc. Abstr. 1905, 88, [i.] 368 ; 1907, 92, [i.] 870), contains *aporeine* $C_{18}H_{16}O_2N$, amorphous ; yielding crystalline salts. Aporeine exercises in frogs a tetanising action similar to that of thebaine. G. B.

RHEIN. 1 : 8 - dihydroxyanthraquinone - 3 - carboxylic acid, *v.* Oesterle (Chem. Zentr. 1912, [i.] 142). Crystallised rhein of commerce consists almost entirely of chrysophanic acid (Oesterle and Hangseth, Arch. Pharm. 1913, 251, 550), *v.* Rhubarb.

RHEONINE *v.* Acridine dyestuffs.

RHEOTANNIC ACID *v.* Tannins.

RHEUMATIN. A preparation of quinine used as an anti-rheumatic. *V.* Salicylic acid and Synthetic drugs.

RHIMBA WAX *v.* Waxes

RHINANTHIN $C_{58}H_{52}O_{40}$. A glucoside found in the seeds of *Rhinanthus Crista-galli* (Linn.), or yellow rattle, and which gives rise to the violet colour occasionally found in rye bread (Ludwig, Zeitsch. Chem. [ii.] 5, 303 ; Arch. Pharm. [ii.] 142, 199 ; Mirande, Compt. rend. 1907, 145, 439). According to Nestler (Ber. deut. bot. Ges. 1920, 38, 117), the colour is due to the formation of *rhinanthocyanin*, by the hydrolysis of the glucoside by means of lactic acid formed during fermentation. It has a nauseously bitter-sweet taste, and crystallises in prisms. Bridel and Braeche are of opinion that 'rhinanthin' is not a distinct substance, but a mixture of aucubin and sucrose (Compt. rend. 1922, 175, 640).

RHODACENE (*quinonoid-peri*-dinaphthylene-naphthalene) a violet-coloured hydrocarbon occurring among the products obtained by passing acenaphthene through a red-hot tube. Best obtained by boiling a 4 p.c. solution of leucacene (*q.v.*) in nitrobenzene, cooling the dark bluish-red liquid, filtering, concentrating the solution under reduced pressure and adding alcohol when rhodacene is precipitated as a dark violet, microcrystalline powder, resembling methyl-violet. M.p. 338°–340°. Its solutions in benzene hydrocarbons resemble those of the red phthaleins, exhibit brilliant red fluorescence and have absorption bands at $\lambda=$ 575–555$\mu\mu$, 535–510$\mu\mu$, 495–475$\mu\mu$, and 460–445$\mu\mu$. The solutions exposed to light gradually become orange-yellow owing to isomerisation to *Chalkacene* (*benzenoid-peri*-dinaphthylene-naphthalene) (Dziewonski and collaborators, Ber. 1920, 53, [B] 2173).

RHODAFORM. Trade name for an addition product of hexamethylenetetramine and methylthiocyanate.

RHODEINE. A hydrocarbon $n(C_{10}H_{16})$ obtained from rosewood oil (Gladstone, Chem. Soc. Trans. [ii.] 10, 3).

The name *Rhodeine* is also given by Jacquernin (Compt. rend. 83, 226, 448) to the characteristic rose colour produced by the successive action of a hypochlorite and a sulphide on aniline.

RHODEOSE *v.* Carbohydrates.

RHODINOL $C_{10}H_{20}O$,

$$Me_2C:CH\cdot CH_2\cdot CH_2\cdot CHMeCH_2\cdot CH_2OH$$

a primary alcohol, is the odorous constituent of otto or oil of roses. It is contained in Turkish and German rose oils, in *Pelargonium odoratissimum* and is also said to occur in the following essential oils : ginger grass, lemon, Turkish palmarosa and neroli (Erdmann and Huth, J. pr. Chem. 1897, 56, 27).

Preparation.—The impure rhodinol obtained by fractionating geranium oil from *Pelargonium odoratissimum* is converted into the acetyl derivative by heating it with acetic anhydride for 8 hours at 140°–145°. The product is cooled,

washed with aqueous alkali, then with pure water and distilled *in vacuô*. The acetyl ester distilling at 127°–132°, is then saponified by solution in alcohol and treatment with an equimolecular quantity of potash. It is allowed to stand for an hour, after which the alcohol is distilled off under diminished pressure; the residue is washed with water, filtered and distilled *in vacuô*, the fraction coming over at 120°–125°, being collected (D. R. P. 80007; Monnet and Barbier, Compt. rend. 1893, 117, 1092). Rhodinol can also be prepared by treating rhodinyl phthalate with sodium chloride, hydrolysing the resulting sodium salt with an alkali and distilling the rhodinol formed in steam (Erdmann, J. pr. Chem. 1897, [ii.] 56, 1); or by treating ethyl rhodinate (obtained from synthetical geranic acid) with sodium ethoxide (Bouveault and Gourmand, Compt. rend. 1904, 138, 1699). In the latter case, the rhodinol formed is racemic, but is otherwise identical with the natural product.

Properties.—Rhodinol is a colourless, oily liquid, b.p. 110·5–111°/10 mm., sp.gr. 0·8812 at 16°/4° (Erdmann, Ber. 1898, 31, 356), b.p. 126·5°/16 mm., sp.gr. 0·8956 at 0°/0° (Barbier, Compt. rend. 1893, 117, 177), sp.gr. 0·8731 at 0°/0° (Barbier and Bouveault, *ibid.* 1896, 529), α_D 2° 34′ at 17°. It is an isomeride of licareol and geraniol, but it has also been regarded as identical with the latter and with *l*-citronellol (Bertram and Gildemeister, J. pr. Chem. [ii.] 49, 285; *ibid.* 1896, [ii.] 53, 225; *ibid.* 1897, [ii.] 56, 506; Ber. 1898, 31, 749; Poleck, *ibid.* 29; J. pr. Chem. 1897, [ii.] 56, 515; Erdmann and Huth, *ibid.* 1896, [ii.] 53, 42; Schimmel, Chem. Zentr. 1898, i. 258).

Rhodinol is probably identical with reuniol (Hesse, J. pr. Chem. 1896, [ii.] 53, 238; Erdmann and Huth, *l.c.*), but not with geraniol or *l*-citronellol.

Rhodinol combines with bromine to form a tetrabromide and with chlorine to form a dichloride (Monnet and Barbier, *l.c.*; Eckart, Arch. Pharm. 229, 355); from the latter, a *terpene*, b.p. 177°–178° has been obtained. When one drop of rhodinol is diluted with 5 c.c. of alcohol and 10 c.c. of concentrated sulphuric acid is then poured in, the acid sinks and becomes of an intense orange colour. On gentle shaking, the surface of contact of the two liquids assumes a reddish-violet colour. Linalool gives a similar reaction, but the colour rapidly turns brown; citronellol under the same conditions, gives a feeble coloration of a bluish tint (Erdmann, J. pr. Chem. 1897, [ii.] 56, 1). When oxidised, rhodinol yields: (1) an aldehyde, *rhodinal* $C_{10}H_{18}O$, mixed with menthone, b.p. of mixture 93°–95°/10 mm. Rhodinal does not combine with sodium bisulphite, but yields an oxime, b.p. 130°–135°/mm. and a semi-carbazone, m.p. 115° (Barbier and Bouveault, Compt. rend. 1896, 122, 529, 737; Bouveault, Bull. Soc. chim. 1900, [ii.] 23, 458, 463). (2) Dimethyl acetone; (3) β-methyl adipic acid. (4) *Rhodinolic acid* or *rhodinylic rhodinate* $C_{20}H_{36}O_2$, b.p. 190°/10 mm. (5) Valeric and possibly other acids (Barbier and Bouveault, Compt. rend. 1894, 119, 334; *ibid.* 1896, 122, 673; Barbier, *l.c.*; Eckart, *l.c.*).

The *rhodinol esters* formed by the action of acid chlorides on rhodinol in the presence of anhydrous pyridine, are liquids the odours of which decrease with increasing molecular weight (Erdmann, Ber. 1898, 31, 356; *see* also Charabot and Hebert, Bull. Soc. chim. [3] 13, 465).

Rhodinol opianate, m.p. 48·5°, is obtained by heating rhodinol with opianic acid at 130°–135° (Erdmann).

Rhodinol pyruvate, b.p. 143°/10 mm., forms a *semicarbazone*, m.p. 112° (Bouveault and Gourmand, *l.c.*).

For other rhodinol derivatives *see* Eckart, *l.c.*; Erdmann, *l.c.*; Erdmann and Huth, *l.c.*

Rhodinol is chiefly employed in perfumery (Pfister, Chem. Zeit. 1897, 38).

RHODIUM. Sym. Rh. At.wt. 102·9. Rhodium is contained in all native platinum and in the nickeliferous copper ores of Sudbury and elsewhere. It is distinguished from the other members of the platinum group by the rose-red colour of its chloride, whence it derives its name, and might be of great importance if obtainable in quantity, on account of the fact that crucibles of rhodium have been found to be practically as resistant in most respects as iridium, whilst having little more than half the specific gravity of that metal (Crookes, Proc. Roy. Soc., 1908). It is, however, attacked by boiling sulphuric acid and dissolved by fused bisulphates with evolution of SO_2. Rhodium is obtained from the solution from which platinum has been precipitated as the double ammonium salt or as potassium chloroplatinate, in which solution it was discovered by W. H. Wollaston in 1804 (Phil. Trans. 94, 419).

The impure metal separated by one of the processes given under Platinum may be purified by a method described in full by Jörgensen (J. pr. Chem. 1855, [2] 27, 433). The metal is alloyed with five times its weight of zinc in the usual way and the button parted in hydrochloric acid leaving the rhodium-zinc alloy as minute needle crystals. This is washed and dissolved in nitric acid or *aqua regia* and ammonium chloride added to precipitate most of the iridium and platinum, if present. Excess of ammonia is added to the filtrate, which is warmed to redissolve the precipitated pink hydroxide, and the whole is evaporated almost to dryness on the water-bath. Hydrochloric acid is added, and the hot filtered liquor on cooling deposits crystals of 'Claus' Salt,' rhodammine chloride $(NH_3)_5RhCl_3$, which may be further purified by recrystallisation.

Rhodium is precipitated in the metallic condition from its solutions by iron. Zinc throws down an alloy or solid solution from which the zinc cannot be completely removed without dissolving the rhodium. The alloys formed by melting lead or zinc with rhodium are described by Debray (Compt. rend. 1880, 90, 1195).

Dilute rhodium chloride with excess of potash gives a colourless solution with which alcohol gives a black precipitate in the cold. This reaction is characteristic and may be used to detect rhodium in platinum solutions.

The melted metal may be tested for its freedom from the other platinum metals by the fact that it is completely dissolved in fused bisulphate of potash, leaving no residue. The melt is deep red while hot, but orange yellow when cold, and the water solution is yellow. Palladium will also dissolve in the fused bisulphate,

but gives a much darker solution from which the metal may be precipitated by boiling ferrous sulphate or other reducing agents which will not reduce rhodium.

Rhodium is a hard, white metal, ductile and malleable at a red heat. It has a sp.gr. of 12·1, fuses at about 1970° and, when pure, is insoluble in *aqua regia*, although it is attacked by chlorine and sulphur. It has the same power as platinum as a catalyst, but has not been commercially applied to that purpose. Its principal use is in the preparation of the thermo-couples for pyrometers, but its employment for the manufacture of crucibles is likely to increase (J. Ind. Eng. Chem. 1911, 3, 354). The thermo-electric properties of the rhodium-platinum element are discussed by Sosman (Amer. J. Sci. 1910, 30, 1); of rhodium-iridium by Broniewski and Hackspill (Compt. rend. 1911, 153, 814). Its salts have not received any technical application.

Colloidal rhodium may be obtained in the same way as colloidal iridium (Gutbier and Hofmeier, J. pr. Chem. 1905, [ii.] 71, 452). It may also be obtained by adding a solution of sodium protalbate to a slightly alkaline solution of the double chloride Na_3RhCl_6, mixed with formaldehyde, when a clear colloidal solution of rhodium is obtained. On dialysis, and subsequent evaporation *in vacuo*, it yields ebony-black plates containing 33 p.c. of rhodium (Zenghelis and Papaconstantinou, Compt. rend. 1920, 170, 1058). The colloidal metal colours a borax bead brown (Donan, Monatsh. 1904, 25, 913). For the catalytic decomposition of formic acid by rhodium *see* Bredig and Blackadder (Zeitsch. physikal. Chem. 1912, 81, 385) and Haas (Zeitsch. Electrochem. 1916, 22, 443).

Rhodium Compounds.

Rhodium forms three oxides :—

Rhodium monoxide RhO is a grey powder, produced when the finely-divided metal is heated in air, or by heating the trihydroxide. It is not attacked by acids, but is reduced by hydrogen with evolution of light. A small quantity of it added to thoria-ceria mantles is said to diminish considerably the amount of ceria required (J. Soc. Chem. Ind. 1897, 37).

Rhodium sesquioxide Rh_2O_3 is formed as a grey iridescent mass by heating the nitrate, or as a crystalline mass when sodium rhodochloride is heated in oxygen. It is insoluble in acids. The corresponding *hydroxide* $Rh(OH)_3$ forms a heavy dark-brown mass when dry. It is almost insoluble in acids, and may be obtained by heating a solution of sodium rhodochloride with excess of caustic potash. If the potash is not in excess, the solution on standing deposits thin yellow crystals of the hydrate $Rh(OH)_3,H_2O$, which is soluble in acid, and, when freshly prepared, in alkalis. If chlorine be passed through the alkaline solution of the yellow salt, the colour changes from yellow to red, then a green precipitate is formed, which dissolves to a deep-blue solution, probably owing to the formation of the *per-rhodate* Na_2RhO_4 (Alvarez, Compt. rend. 1905, 140, 1341). The rhodium salts are derived from this oxide ; they are of a dark red or yellow colour, and have a bitter taste.

According to Gutbier (Zeitsch. anorg. Chem. 1916, 95, 225) rhodium sponge heated in air to 600°/1000° always gives Ru_2O_3 ; above 1150° the oxide decomposes, leaving the metal. The lower oxides previously reported were only due to incomplete oxidation.

Rhodium dioxide RhO_2, which closely resembles the sesquioxide, is obtained by repeated fusion with caustic potash and potassium nitrate. The corresponding tetrahydroxide $Rh(OH)_4$ is formed by the action of chlorine on the trihydroxide. It forms a green powder which yields a blue solution in hydrochloric acid, the colour gradually changing to red with evolution of chlorine.

Rhodium trichloride $RhCl_3$ may be obtained by heating the metal in chlorine, or from the crude double chloride $RhCl_3{\cdot}3NaCl$ (formed by the action of chlorine on the metal in the presence of sodium chloride) by saturating its aqueous solution with hydrogen chloride, thus precipitating the sodium chloride, then evaporating the residue in a current of chlorine (Leidié, Compt. rend. 1899, 129, 1249). It may also be obtained by evaporating the dioxide with hydrochloric acid (Gutbier and Trenkner, Zeitsch. anorg. Chem. 1905, 45, 166), and by other methods. Its colour and properties depend on its mode of preparation. It forms a large number of well-crystallised *rhodochlorides* or *chlororhodites* of the type M_3RhCl_6,xH_2O and also M_2RhCl_5,xH_2O (Gutbier and Trenkner, *l.c.* ; Gutbier and Hüttinger, Ber. 1908, 41, 210).

The sodium salt $Na_3RhCl_6,9H_2O$ effloresces in dry air and melts at 50° in its own water of crystallisation. It is insoluble in alcohol. By mixing strong hot solutions of the above salt and ammonium chloride and allowing the solution to cool, prisms and hexagonal plates of $(NH_4)_2RhCl_5,H_2O$ are deposited. The mother liquor on slow evaporation in the cold deposits large dark-red prisms of $2(NH_4)_3RhCl_6,3H_2O$, which are more soluble in water than the former. Both are insoluble in alcohol.

Excess of caustic potash added to a dilute solution of $RhCl_3$ or a double salt causes no precipitate, but the colour gradually turns yellow. The addition of alcohol at ordinary temperatures causes a black precipitate, characteristic of the metal.

The tribromide and iodide and their double salts have also been prepared (*see* above references and Goloubkine, Bull. Soc. chim. Belg. 1910, [ii.] 24, 388).

Rhodium monosulphide RhS, a bluish-white mass with a metallic lustre, is obtained by heating the metal in sulphur, or by passing sulphuretted hydrogen through a solution of a rhodium salt. If the latter process is carried out at 100°, the hydrosulphide $Rh(SH)_3$ is formed (Leidié, Compt. rend. 1888, 106, 1533).

The **sesquisulphide** Rh_2S_3 forms black crystalline plates produced by treating the trichloride with sulphuretted hydrogen at 360°.

Rhodium sulphate $Rh_2(SO_4)_3$ and the **sulphite** $Rh_2(SO_3)_3$ have also been obtained.

Rhodium forms alums with the alkali metals, of the type $M_2SO_4,Rh_2(SO_4)_3,24H_2O$ (Piccini and Marino, Zeitsch. anorg. Chem. 1901, 27, 62).

Rhodium nitrate $Rh(NO_3)_3$, **nitrite** $Rh(NO_2)_3$, and its double salts, also **potassium rhodicyanide** $K_3[Rh(CN)_6]$, are known (Leidié, Compt. rend. 1890, 111, 106 ; 1900, 130, 87).

Rhodium forms several series of ammoniacal derivatives, of which the three chief are :

Hexammine salts (Luteo salts)
$[Rh(NH_3)_4]X_3$,
Aquopentammine (Roseo salts)
$[RhH_2O(NH_3)_5]X_3$,
Pentammine (Purpureo salts)
$[RhX(NH_3)_5]X_2$,
where X is a negative radical. These salts resemble the corresponding cobalt salts.

The following twenty-four complex salts of rhodium chloride and organic ammonium chlorides are known:—

A. *Hexachlororhodiates* of the general formula $[Rh(Cl_6)](NR_4)_3$; *dimethylammonium*, red, monoclinic; *trimethylammonium*, transparent, reddish-brown; *ethylammonium*, garnet; *diethylammonium*, garnet; *triethylammonium*, dark red, monoclinic; n-*propylammonium*, carmine; iso*propylammonium*, garnet; *dipropylammonium*, dark red; *tripropylammonium*, carmine, monoclinic; n-*butylammonium*, light red; iso*butylammonium*, carmine; *di*iso*butylammonium*, light red, monoclinic; *guanidinium*, carmine, monoclinic; *propylenediammonium*, carmine; *pyridinium*, orange-red, monoclinic; B-*picolinium*, orange-red; *lutidinium*, orange-red; *collidinium*, red, monoclinic; *quinolinium*, red, monoclinic; iso*quinolinium*, dark red, monoclinic.

B. *Tetramethylammoniumtrichlorohexachlorodirhodiate*, brown, hexagonal, and the *tetraethylderivative*, reddish-brown, monoclinic; these two have the formulæ $[Rh_2Cl_9](NR_4)_3$.

C. *Dichlorotetra - methylammoniumchloride-rhodichloride* $[Cl_2Rh(NH_3MeCl)_4]Cl$, dark red, hexagonal. *Dichlorodi - ethylenediammonium chloride-rhodichloride* $[Cl_2Rh(C_2H_4N_2H_6Cl_2)_2]_2Cl$, brick-red, tetragonal. Details of preparation of the above compounds and of rhodium chlorides are given, as well as methods for the recovery of rhodium from the residues (A. Gutbier and H. Bertsch, Zeitsch. anorg. Chem. 1923, 129, 67782; Chem. Soc. Absts. 1923, 123, 124, i. 1184). A. J. W.

RHODIZITE. Borate of aluminium, glucinum, and alkalis, crystallised in the cubic system with tetrahedral development. Two analyses of crystals from Madagascar gave the formulæ $B_{14}Al_6Gl_7(Li,K,Cs,Rb,Na,H)_4O_{39}$ and $B_{12}Al_6Gl_4(Li,K,Na,H)_8O_{35}$, with GlO 14·93 and 10·10 p.c., Li_2O 0·68 and 7·30 (?), Cs_2O 3·47, Rb_2O 2·29, K_2O 1·41 (K_2O+Cs_2O 5·90), Na_2O 1·78 and 3·30 p.c., respectively. For many years it was known only as minute colourless crystals encrusting rubellite (red tourmaline) from the Urals. In 1909 and 1911 larger crystals of a pale yellowish-green colour were found at two localities in Madagascar, where it occurs with gem-minerals (rubellite and kunzite) in pegmatite. Sp.gr. 3·305–3·344. The high degree of hardness (H.=8) is exceeded by but few gem-minerals; crystals from Madagascar have been cut as gems. Refractive index (Na) 1·69. Before the blowpipe it colours the flame at first green and then red, and it is fusible with difficulty to a white glass. It is unattacked by all acids. The crystals are pseudo-cubic, and show the same optical anomalies and pyro-electric characters as boracite. L. J. S.

RHODIZONIC ACID *v.* KETONES.

RHODOCHROSITE, or Manganese-spar. Native manganese carbonate $MnCO_3$ (47·7 p.c. manganese), crystallising in the rhombohedral system and isomorphous with calcite. Its characteristic colour is rose-red, hence the name rhodochrosite (not rhodochroisite), from *ῥόδο-χρως*; another name in common use is dialogite —often misspelt 'diallogite.' Occasionally the colour is yellowish-grey or brown, due to the presence of iron; calcium, magnesium, zinc, or cobalt may also be present isomorphously replacing manganese. With these variations in composition the sp.gr. ranges from 3·0 to 3·6. In appearance, rhodochrosite somewhat resembles rhodonite (*q.v.*), from which it may be readily distinguished by its inferior hardness (H.=4) and by the fact that it effervesces in warm hydrochloric acid. The mineral usually occurs as granular or sparry masses showing a perfect rhombohedral cleavage, but occasionally crystals are found. These often have the form of rhombohedra with curved faces. Small clear crystals of scalenohedral habit are found in cavities in limonite near Horhausen in Rhenish Prussia; and magnificent rhombohedra associated with iron-pyrites come from Alicante, in Lake Co., and other localities in Colorado.

Rhodochrosite occurs in mineral-veins, together with ores of lead and silver; and as veins and beds in limestone. The most important deposit is that worked in limestone at Las Cabesses mine (dep. Ariège) in the Pyrenees, the output amounting to about 6000 tons per annum. It is also mined near Vielle Aure (dep. Hautes-Pyrénées), occurring there also in limestone and intimately intermixed with rhodonite and other manganese silicates. A bed, 10–20 inches in thickness, of mixed rhodochrosite and rhodonite weathering to pyrolusite occurs interstratified with Cambrian grits in the Llanbedr district in Merionethshire. Ferriferous rhodochrosites ('ponites') of variable composition constitute the primary manganese and iron ores in the crystalline rocks near Brosteni in Rumania, and by their alteration give rise to manganites of manganese and iron ('brostenites'). Rhodochrosite is used for the manufacture of ferromanganese and spiegeleisen. When occurring with silver ores, as in Colorado and Montana, it is of value as a flux. L. J. S.

RHODODENDRIN. A glucoside $C_{16}H_{22}O_7$, found in the leaves of *Rhododendron chrysanthum* (Pall.). It is soluble in water, has a bitter taste, and melts at 187°.

RHODODENDROL $C_{10}H_{12}O_2$, a camphor-like decomposition product of rhododendrin, forms long colourless needles melting at 80° and subliming without decomposition (Archangelski, Chem. Zentr. 1901, [ii.] 594).

RHODOLITE *v.* GARNET.

RHODONITE. Native manganese metasilicate, $MnSiO_3$, crystallising in the anorthic system and belonging to the pyroxene group of minerals. (Another native manganese silicate is the orthosilicate, Mn_2SiO_4, called tephroite and belonging to the olivine group; several other mineral silicates contain manganese in combination with other metallic bases.)

Rhodonite, so named from *ῥόδον*, a rose, is typically of a rose-red colour, and usually forms granular to compact masses, with sp.gr. 3·5–3·6 and hardness 6. Such material is of value,

when cut and polished, for ornamental purposes. The best quality is that quarried in black clay-slates at Sedelnikova, near Ekaterinburg on the eastern slopes of the Urals. Boulders of similar material are found near Cummington in Massachusetts; and small blocks have been obtained in the Treburland mine and other manganese mines near Launceston in Cornwall. The invariable presence of veins and splashes of black manganese oxide (produced by the partial alteration of the material) form a pleasing contrast with the rich rose-red colour of the polished stone. Small brilliant crystals of rhodonite are found in the manganese mines at Filipstad in Sweden; and large rough crystals (of a zinciferous variety called fowlerite) are known from the zinc mines at Franklin Furnace in New Jersey. Well-formed crystals and grains occur embedded in galena at Broken Hill in New South Wales. In the Pyrenees compact masses of rhodonite intimately intermixed with other manganese silicates and with rhodochrosite from beds in limestone; this material is mined (about 5000 tons per annum) at Vielle Aure (dep. Hautes-Pyrénées) for the manufacture of ferromanganese and spiegeleisen. Rhodonite is also used to a limited extent in pottery glazing and as a flux in smelting. L. J. S.

RHOTANIUM. An alloy of gold with varying proportions of palladium used as a substitute for platinum in the manufacture of crucibles, evaporating dishes, &c. Used also in jewellery work, dentistry, electrical instruments, &c. Rhotanium A (10 p.c. of Pd) is superior to platinum in respect to its resistance to loss on heating, compares favourably with platinum in resistance to boiling hydrochloric and hydrofluoric acids, to boiling 20 p.c. sodium hydroxide, to fusion with sodium carbonate and with potassium pyrosulphate. It is superior to platinum in resistance to boiling sulphuric acid, but inferior in its resistance to nitric acid, boiling ferric chloride solutions and for fusions with sodium hydroxide. The low m.p. of the alloy is a disadvantage (Gurevich and Wichers, J. Ind. and Eng. Chem. 1919, [ii.] 570; Analyst, 1919, 303).

RHUBARB, *Rheum officinale* (Baill.), and other species. A plant grown in the East for the sake of its rhizome, which is used in medicine (*v.* RHUBARB-ROOT), in temperate climates for the young stems which are used for table purposes. According to König, the following figures show the average composition of the edible stems—

	Water	Protein	Fat	Sugar	Other N-free subst.	Crude fibre	Ash
Large sticks	95·2	0·5	0·6	0·3	2·2	0·6	0·6
Small sticks	93·8	0·5	0·6	0·1	3·8	0·6	0·7

The large sticks contained 1·09 p.c. oxalic acid; the small, 0·5 p.c. According to Castoro (Landw. Versuchs. Stat. 1902, 56, 423), malic acid is also present in the stems. Calcium oxalate is found in the stems.

Quantities of rhubarb are grown in the neighbourhood of large towns, finding a large sale as a substitute for fruit, especially in the spring and early summer. Much of the rhubarb is 'forced' by being grown with the aid of heat, and is partially etiolated by whole or partial exclusion of light. In the open, crops up to 40 or 50 tons per acre of 'sticks,' can be grown by liberal nitrogenous manuring (*v.* Dyer and Shrivell, Jour. Royal Hort. Soc. 1903, 27, part 4). The quality of the product, especially its tenderness and succulence, is greatly enhanced by the use of sodium nitrate. When rhubarb is 'forced' by digging up the roots, keeping them in the cold until about Christmas and then placing them in darkened houses kept at about 60°–65°, much earlier and larger growth can be secured by first exposing the roots to ether vapour (10 c.c. ether per cubic foot of air) for 48 hours, before placing in the hothouse (Stuart, Rep. Vermont. Agric. Expt. Stat. 1903–1904, 442).

Rhubarb juice is used in the manufacture of a wine. The following results were obtained from the analyses of seven samples:

Total solids 23·45–35·25; reducing substances 4·5–12·7; ash 4·1–6·9; ammonia-nitrogen 0·13–0·45; protein-nitrogen 0·05–0·22; oxalic acid 2·11–3·53; tannin 0·06–0·38 grm. per litre; total acidity 154·5–222·0 c.c.; alkalinity of ash 42·0–82·8 c.c.; and free organic acids 150·4–217·3 c.c. of N/1 solution (Besson, Schweiz. Ver. anal. Chem. 1918).

Angerhausen (Zeitsch Unters. Nahr. Genussm. 1920, 39, 122) gives the following results of the analysis of rhubarb (stalk) juice: Sp.gr. 1·0187–1·0237; total solids 3·69–4·96 p.c.; total sugar (as invert sugar) 1·21–2·08; ash 0·62–0·77; oxalic acid 0·23–0·32; citric acid 0·08–0·24; malic acid 2·0 p.c.; free acidity (c.c. N/1 acid) 26·5–29·6. Free oxalic acid is not present in the juice. The free acidity decreases when the juice is fermented, and the whole of the combined oxalic acid may be removed by treatment with calcium carbonate. H. I.

RHUBARB RESIN *v.* RHUBARB-ROOT.

RHUBARB-ROOT (*Rheum*, U.S. Pharm.; *Rhei Rhizoma*, Brit. Pharm; *Rhubarbe*, Fr.; *Rhabarber*, Ger.). The rhizome of *Rheum palmatum* (Linn.), *Rheum officinale* (Baillon), and possibly other allied species, all inhabitants of Central Asia. For botanical characters *v.* Bentl. a. Trim. 213, 214; Flück. a. Hanb. 491; Pereira (Mat. Med. 1850, 2, 1343); also Flückiger (Neues Rep. Pharm. 25, 1), and Baillon (Pharm. J. [iii.] 3, 301). Attempts have been made from time to time to cultivate the official rhubarb plants in Europe which have been attended with a certain amount of success. Other allied species have also been grown. These have supplied the market with substitutes for the Chinese drug. The most important are *R. Rhaponticum* (Linn.), cultivated for a century in the neighbourhood of Banbury, and the same species, together with *R. palmatum* (Linn.), *R. undulatum* (Linn.), and *R. compactum* (Linn.), which are grown in France and Germany. The comparative value of English rhubarb has been studied by H. Senier (Pharm. J. [iii.] 8, 444) and Elborne (*ibid.* [iii.] 15, 136).

Rhubarb has been known from the very earliest time as a mild purgative and stomachic. Not only was its value appreciated by Dioscorides, but in China its history goes back to the reign of the Emperor Shen-Nung, B.C. 2700. With the advent of chemical inquiry at the beginning of this century the composition of rhubarb was studied by numerous investigators. Of their results a summary is given by Pereira (Mat. Med., 1850, 2, 1355), but, with the exception of

the identification of constituents which are common to most plants, this early work only resulted in the preparation of active but chemically indefinite extractives.

The first chemical investigation to give definite results of physiological importance was that of Schlössberger and Döpping (Annalen, 1844, 50, 213). These observers isolated *chrysophanic acid*, a yellow crystalline colouring agent which had already been found in the wall-lichen by Rochleder and Heldt (*ibid.* 48, 12), and which Liebermann (*ibid.* 183, 145) has shown to be a derivative of anthraquinone. Chrysophanic acid has also been obtained from the lichen *Parmelia parietina*, from *Squamaria elegans* (Thomson, *ibid.* 53, 260), *Rumex obtusifolius* (Linn.) (Thann, *ibid.* 107, 324), *Rumex Ecklonianus* (Meissner) (Tutin and Clewer, Chem. Soc. Trans. 97, 1), from goa-powder of *Andira Araroba* (Aguiar), and from the bark of *Cassia bijuga*, *Rhamnus Frangula* and *Rh. Purshiana*. De la Rue and Müller (Chem. Soc. Mem. 1857, 10, 298) discovered another crystalline colouring matter of a darker red-orange colour, *emodin*. This compound has also been found in the bark of *Rhamnus Purshiana* (De Cand.), (Cascara), and of *Rhamnus Frangula* (Linn.) (as the glucoside frangulin), in other species of *Frangula* (Tschirch and Pool, Arch. Pharm. 1908, 246, 315; Tschirch and Polacco, *ibid.* 1900, 238, 459), and in *Polygonum cuspidatum* (as the glucoside polygonin). According to Kubly (Pharm. Zeit. 6, 603; 24, 193; Pharm. J. [iii.] 16, 65) chrysophanic acid does not exist to any appreciable extent in rhubarb-root, but is produced by the fermentation, in presence of water, of a glucoside *chrysophan*. This view is confirmed by Dragendorff (*ibid.* [iii.] 8, 826). *Cf.* also Wasicky (Ber. deut. botan. Ges., 1915, 33, 37), who shows that crystals of a hydroxymethylanthraquinone appear in the root after injury, owing to an enzyme hydrolysing the glucoside.

Many substances have been isolated from rhubarb by different workers. Most of these, however, are probably mixtures, and different names have been given to substances according to the state of purity in which they have been isolated. Among the more recent workers on this subject are Hesse (Annalen, 284, 191; 309, 32; J. pr. Chem. [ii.] 77, 32, 383); Tschirch and co-workers (Arch. Pharm. 240, 596; 243, 443; 245, 139; Chem. Zentr. 1904, i. 1077; 1095, ii. 144); Eyken (Pharm. Weekblad, 1904, 41, 177); Gilson (Compt. rend. 136, 385; Arch. internat. Pharmacod. Thér. 1905, 14, 487).

Among other substances, Chinese rhubarb contains *chrysophanic acid*, *aloe-emodin* (rhabarberon of Hesse, *iso*-emodin of Tschirch and Eyken), *emodin monomethylether* (Oesterle and Johann, Arch. Pharm. 248, 476); *emodin* which is identical with the emodin obtained from frangula; and *rhein;* for constitution and properties of these substances *see* below. Rhubarb also contains a mixture of glucosides of anthraquinone derivatives, which may be crystallised. Gilson (*l.c.*) isolated *chrysophanein* $C_{21}H_{20}O_9$, m.p. 242°–249°, and *rheochrysin* $C_{22}H_{22}O_{10}$, m.p. 204°, which have been shown to be the glucosides of chrysophanic acid and emodin monomethyl ether respectively. *R. Rhaponticum* contains *rhapontin* (*rhaponticin*) $C_{21}H_{24}O_9$, m.p. 231°, with compounds similar to those found in Chinese rhubarb, but rhein and emodin are not present. From *R. palmatum*, there have been isolated emodin, aloeemodin, and rhein, and from *R. officinale* (Baillon) the same compounds with the exception of emodin.

An examination of Shensi rhubarb has been made by Tutin and Clewer (Chem. Soc. Trans. 1911, 99, 946). An alcoholic extract of the drug, when distilled with steam, yielded small amounts of palmitic and chrysophanic acids together with a hexoic acid and some essential oil. The portion of the extract which was soluble in water yielded cinnamic acid, gallic acid 2·2 p.c., rhein 0·12 p.c., emodin 0·78 p.c., aloe-emodin 0·16 p.c., emodin monomethylether 0·22 p.c., chrysophanic acid 0·49 p.c., crystalline mixture of glucosides of anthraquinone derivatives 2·0 p.c., tannin 0·52 p.c., non-glucosidic resin 10·4 p.c., and a new substance, *rheinolic acid*, $C_{17}H_{10}O_6$, m.p. 295°–297°, 0·003 p.c. What proportion, if, any, of the anthraquinone derivatives occur in the root uncombined with sugar, is doubtful.

Tutin and Clewer obtained an apparently homogeneous glucoside with constant m.p. 235°, but on hydrolysis this yielded both chrysophanic acid and emodin monomethylether. They regarded it as an inseparable mixture of chrysophanein and rheochrysin of Gilson.

The resin on hydrolysis gave small quantities of gallic and cinnamic acids, rhein, emodin, aloe-emodin, emodin-monomethyl-ether, and chrysophanic acid with a new compound $C_{14}H_{12}O_3$, m.p. 256°, probably a *trihydroxydihydroanthracene*. The portion of the extract insoluble in water yielded a trace of a *hydrocarbon*, m.p. 64°; a phytosterol (verosterol), $C_{27}H_{46}O$; a mixture of fatty acids; rhein, rheinolic acid, emodin, aloe-emodin, emodin-methyl-ether, chrysophanic acid.

Of the anthraquinone derivatives only aloe-emodin and chrysophanic acid were found to have any purgative action, the mixture of glucosides being quite inert. The chief purgative principle is the non-glucosidic resin. Other workers, however, considered the glucosides to be active. According to Tschirch there are two kinds: anthra-glucosides (*e.g.* chrysophanein, and rheochrysin of Gilson), which have a purgative action, and tanno-glucosides which have the opposite effect. Of the latter Gilson (Compt. rend. 1903, 136, 385) isolated *glucogallin* $C_{13}H_{16}O_{10}$, m.p. 200°–205°, a glucoside of gallic acid, and *tetrarin* $C_{32}H_{32}O_{12}$, m.p. 204°–205°, which is hydrolysed to equimolecular proportions of glucose, cinnamic acid, gallic acid, and *rheosmin* $C_{10}H_{12}O_2$, m.p. 79·5°, a phenolic aldehyde.

Rheum Rhaponticum has been examined by Gilson (*l.c.*), by Tschirch and Christofoletti (Arch. Pharm. 1905, 243, 443), and by Hesse (J. pr. Chem. 1908, [ii.] 77, 321). It contains the glucoside *rhapontin* $C_{21}H_{21}O_3(OCH_3)$, prisms, m.p. 231°, hydrolysed by acids to glucose and *rhapontigenin* $C_{16}H_{17}(OCH_3)(OH)_2$, m.p. 180°–181°.

Müller (Chem. Soc. Trans. 1911, 99, 967) finds that rhubarb also contains alizarin.

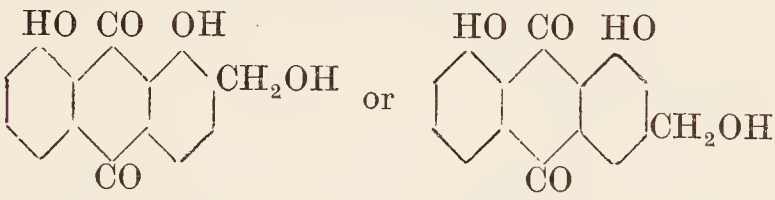
A method for the valuation of rhubarb based on the amount of chrysophanic acid that can be obtained from it has been examined by Tschirch and Edner (Arch. Pharm. 1907, 245,

150). They found the following percentages of acid in the different varieties of rhubarb: Canton round, 3·9; Shanghai, 3·8; Canton flat, 3·0; Shensi flat, 3·0 and 2·7; Shanghai flat, 2·7; Canton II., 2·5; English, 2·0; French, 1·9; Austrian, 1·6.

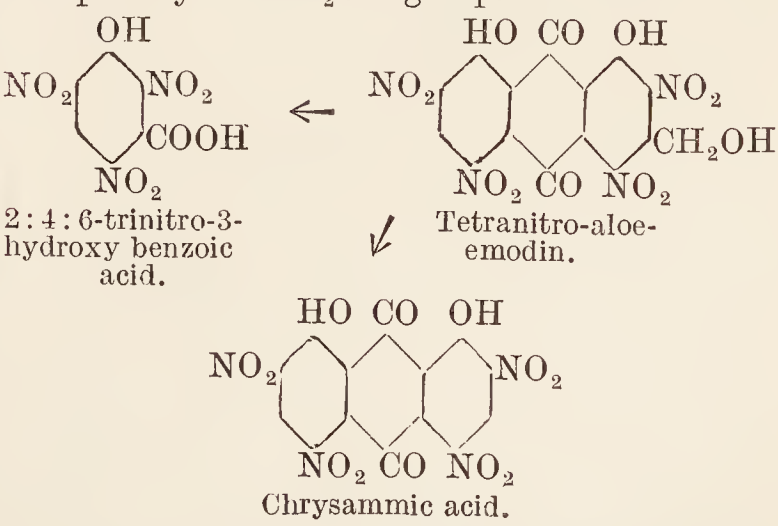
The methods hitherto adopted for the assay of rhubarb depend upon the assumption that the anthraquinones or their glucosides are the important active constituents. The glucosides, however, are more purgative than the free anthraquinones, and to allow for this difference the free anthraquinones and the combined anthraquinones have been determined separately. There is also the possibility that all the four anthraquinone-glucosides that are known to exist in the plant vary in their action. Further, these glucosides have only about one-fourth to one-half the activity of the drug, and comparatively large quantities would have to be administered to produce purgative action. P. Casparis and H. Göldlin (Schweiz. Ap. Ztg. 61, 389) have attempted to gain an insight into the relative purgative action of different varieties of the drug and its preparation by means of physiological experiments. They began by extracting one and the same sample of rhubarb by different methods, using 45 or 90 p.c. alcohol, boiling or percolating, &c. They found little difference in the yield of dry extract, but 45 p.c. alcohol exhausted the drug much more easily than 90 p.c. The dried extracts were dissolved in water or made into an emulsion with mucilage and water, and definite quantities introduced directly into the stomachs of white mice, which served for the experiments. One result of the experiments was to show that extracts obtained by evaporation *in vacuô* were about four times as active as those obtained by evaporation under ordinary pressure. There was no difference between the extracts made with 45 p.c. alcohol and those made with 90 p.c. alcohol, but the former is more economical; for the purpose of extraction, maceration is as effective as percolation and quicker. Very little difference in activity was found between Shensi rhubarb and the rhizome or root of *R. palmatum foliis purpureis* cultivated in Munich, nor is the difference in activity proportionate to the yield of extract. The anthraquinones in these three rhubarbs were then determined by the methods of Daels and of Tschirch. It was found that the activity of the extracts prepared under ordinary pressure in no way corresponded to the amount of anthraquinones in them, and also that there were discrepancies between the physiological action of the other extracts and the amount of anthraquinones contained in them. Of the chemical methods of assaying rhubarb, that of Daels gave results most nearly corresponding with those obtained by physiological experiment, but in the case of extracts not prepared *in vacuô* the method of Daels also failed (Pharm. J. 1924, 112, 6).

The constitution of the various anthraquinone derivatives referred to above has of late been established with great probability and their relationship may well be discussed here. Reference should also be made to the articles on aloes, cascara, chrysarobin, and senna, which drugs all contain some of these anthraquinone derivatives.

Chrysophanic acid is a methyldihydroxy anthraquinone (hence chrysophanol is a more scientific name). It can be obtained by reduction of aloe-emodin (Oesterle and Riat, Arch. Pharm. 1911, 249, 445), which contains an additional hydroxyl, in the methyl group. In *rhein* this methyl group is replaced by a carboxyl group. Rhein is obtainable from both chrysophanol and aloe-emodin by oxidation. Chrysophanol, aloe-emodin, and rhein are therefore related as hydrocarbon, primary alcohol, and carboxylic acid. The presence of a carboxyl group in rhein was overlooked until Robinson and Simonsen (Chem. Soc. Trans. 1909, 95, 1085) replaced it by hydrogen in dimethyl rhein (through the amide, amine, and diazotisation). Chrysophanic acid and aloe-emodin yield β-methyl anthracene on distillation with zinc-dust. Aloe-emodin is oxidised by nitric acid, with elimination of the CH_2OH group, to chrysammic acid or tetranitrochrysazin, which has the two phenolic hydroxyls in positions 1 and 8. Hence aloe-emodin is represented by either of the following formulæ:



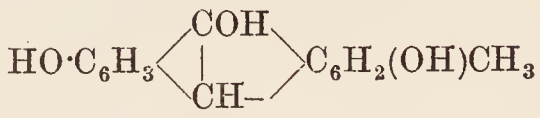
In choosing between positions 2 and 3 for the side chain the only element of uncertainty arises. Oesterle (Arch. Pharm. 1911, 249, 445) first preferred position 2, but later (Arch. Pharm. 1912, 250, 301) abandoned this for position 3, because when the carboxyl group of rhein is replaced by a phenolic hydroxyl, the resulting trihydroxy anthraquinone, m.p. 277°–278°, is not identical with the 1 : 2 : 8 derivative. He thereby came into agreement with Fischer, Falco, and Gross (J. pr. Chem. 1911, [ii.] 84, 369), and Léger (Compt. rend. 1911, 153, 114; 1912, 154, 281). The latter bases his conclusions on the production of both chrysammic acid and 2 : 4 : 6-trinitro-3-hydroxybenzoic acid from tetranitro aloe-emodin, whence it follows that the 2-position is occupied by a nitro group in tetranitro aloe-emodin, and cannot be occupied by the CH_2OH group.



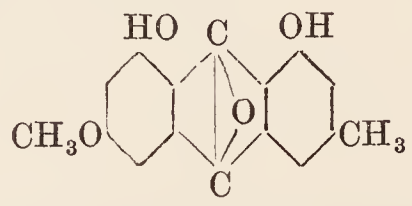
The 3-position of the methyl group in chrysophanic acid also follows from the production of 5-hydroxy-*iso*-phthalic acid by potash fusion. *Emodin* (Frangula-emodin) is a trihydroxymethylanthraquinone closely related to chrysophanic acid, from which it differs by an additional hydroxyl group, probably in the 7-position (*cf.* Oesterle and Sypkens-Toxopéus.

Arch. Pharm. 1911, 249, 311). One or more of its monomethylethers occurs also in a number of plants (*e.g.* Perkin, Trans. Chem. Soc. 1907, 91, 2074).

The above methyl-anthraquinones occur frequently in the form of glucosides (*e.g.* in rhubarb) and sometimes as reduction products (the so-called anthranols), particularly in chrysarobin. The anthranol of chrysophanic acid, for instance, has the constitution



An intermediate stage of reduction is shown by dehydroanthranol of emodin monomethyl-ether, also present in chrysarobin.



Chrysophanic acid forms golden-yellow needles, m.p. 196°, insoluble in sodium carbonate; its diacetyl derivative and its dibenzoyl derivative both melt at 204°. (Frangula) Emodin forms orange-red needles, is soluble in sodium carbonate, and melts at 255°, its triacetyl derivative at 196°, its tribenzoyl derivative at 186°. Aloe-emodin forms orange-red needles melting at 223°; its triacetyl derivative melts at 170°, its tribenzoyl derivative at 232°. Rhein is very little soluble in organic solvents (except aniline, pyridine, &c.), forms glistening orange-yellow needles, m.p. 318°; diacetyl rhein melts at 258°, dibenzoyl rhein at 262°; these acyl derivatives are readily soluble in sodium carbonate. Emodin monomethylether melts at 200°, its diacetyl compound at 186°, its dibenzoyl compound at 228°.

Various synthetical anthracene derivatives have been recommended as purgatives, *e.g.* 1 : 8-dihydroxyanthraquinone, diacetylisopurpurin (1, 2, 7-trihydroxyanthraquinone), and a mixture of methyl ethers of rufigallic acid (a hexahydroxyanthraquinone).

E. Maurin (Bull. d. Sci. Pharm. vol. 30, 337) has determined the percentage of combined and free oxymethylanthraquinones in commercial varieties of rhubarb with the following results :—

——	Combined	Free	Total
Shensi flat . .	3·75	0·60	4·35
Shensi round . .	3·00	1·50	4·50
Canton flat . .	2·60	0·55	3·15
Canton round . .	2·35	0·65	3·00
Hongkong flat . .	4·00	0·50	4·50
Shanghai round .	1·60	1·45	3·05
Austrian flat . .	2·00	1·25	3·25
Austrian round .	1·50	0·90	2·40
English flat . .	2·25	0·80	3·05
R. rhaponticum round	2·30	1·20	3·50
R. Emodi round .	1·60	0·85	2·45

The tincture made from the flat Shensi root, assaying 4·35 p.c. of total oxymethylanthraquinones, showed on examination that only 3·00 p.c. was extracted, and the extract only contained 1·80 p.c., there being therefore a considerable loss.

The cessation of the importation of Chinese rhubarb into Germany during the war led to renewed attention being paid to the cultivation of *Rheum palmatum* (Linn.), and *R. officinale* (Baill), in Europe, and particularly in Germany. The seeds of the former plant were obtained for this purpose from Prof. Tschirch, in Bern, and the cultivation of both species was prosecuted with great zeal by Prof. Ross, of Munich. Tschirch had come to the conclusion that the rhizomes of *R. palmatum* and *R. officinale* obtained from plants cultivated in England and France were not equal to the Chinese drug and were chemically of less value; this he ascribes to the fact that in China the plants grow at an altitude of 12,000 to 14,000 ft. Ross cultivated the plants at more than 100 localities in Germany, and found that, contrary to Tschirch's opinion, the plants did not thrive so well at altitudes between 2000 and 3000 metres as they did at lower heights. At 1800 metres they grew slowly; cultivated plants always yielded a good drug. Both Ross and Tschirch gave the preference to *R. palmatum*, as that is the species that yields the most valuable commercial rhubarb (Shensi), grows more quickly, and is easily distinguished from *R. rhaponticum* (Linn.). Semmler grew the same species in Russia, and found that the plants yielded the best drug when three or four years old, and that in respect of the amount of oxymethylanthraquinones present the cultivated drug was not only equal but even superior to the best Chinese rhubarb. The valuation of rhubarb as at present carried out depends upon the determination of the extract, ash, and percentage of oxymethylanthraquinones. As regards the extract and oxymethylanthraquinones, L. Kroeber found that the roots of plants cultivated near Munich contained appreciably more than the rhizomes, and that therefore the separation of the roots and even the parings of the rhizomes was a waste of material. *R. officinale* was in both respects better than *R. palmatum*. The percentage of oxymethylanthraquinones may be determined colorimetrically, spectroscopically, or gravimetrically, but the real value of a rhubarb depends upon its activity rather than upon any theoretical considerations. When put to the practical test no difference could be detected between the two species cultivated by L. Kroeber when doses of 1 grm. were administered. This is, however, too large a dose. It appears that the percentage of anthraquinone derivatives present is not in direct proportion to the activity of the drug. *R. palmatum* contains appreciably less anthraquinones than *R. officinale*, but in activity the former far surpasses the latter. *R. palmatum* with 2·268 p.c. of anthraquinones was much more active than *R. officinale* with 3·937 p.c. There is therefore undoubtedly some difference in the active constituents of these two drugs. Possibly an explanation is to be found in the fact that Eijken found no emodin in the rhizomes and roots of *R. officinale* cultivated in Bern. Powdered *R. palmatum* was boiled with dilute sulphuric acid and chloroform under a reflux condenser for 2½ hours (as is done in the determination of the oxymethylanthraquinones) and

the chloroform solution of the oxymethylanthraquinones separated. The extracted powder, when tested for its therapeutical action, was found to have just the same action as it had before extraction. As emodin is difficultly soluble in chloroform, it may be assumed that a considerable proportion of that present in the original drug was left in the powder after extraction. The result of this experiment throws much doubt on the reliability of the method of estimating the activity of rhubarb by determining the percentage of oxymethylanthraquinones obtainable from it. These results were confirmed by exhausting powdered rhubarb with chloroform, which removed the free oxymethylanthraquinones, then boiling with dilute sulphuric acid and chloroform, separating the chloroform solution, washing the residual powder with water until free from oxymethylanthraquinones (which occupied several days), and then drying. The powder thus exhausted acted as a satisfactory laxative with four persons out of the five on whom it was tried. Although these experiments, owing to the small number of persons on whom they were tried, are not conclusive, they indicate that the determination of the oxymethylanthraquinones in rhubarb is solely of theoretical interest (L. Kroeber, Schweiz. Apoth. Ztg. vol. 61, 221).[1] G. B.

RHYOLITE or Liparite. A volcanic rock of the most acid type corresponding with the plutonic granite. In chemical and mineral (except in the glassy forms) composition they are similar to granite, quartz-porphyry, obsidian, and pumice, differing essentially from these in texture. The average composition is: SiO_2 76·4, Al_2O_3 12·0, Fe_2O_3+FeO 2·0, CaO 1·1, MgO 0·6, K_2O 3·7, Na_2O 4·5; sp.gr. 2·55. They are fine-grained rocks usually of a light grey colour, but ranging from pure white to dark grey, and often showing porphyritic, spherulitic, flow (hence the name, from ῥύαξ, stream, and λίθος, stone), and cellular structures. The minerals present are quartz and potash-felspar (sanidine) with ferro-magnesian minerals only in small amount. Some glassy base is usually present, forming a passage to obsidian; but in the more ancient rhyolites this has become devitrified and stony, as in the rocks generally known as felsites. Rhyolites are of wide distribution both in space and time. They are abundant in Hungary, Germany, Lipari Islands (hence the name liparite), &c. In the British Isles a typical rhyolite of Tertiary age occurs at Tardree in Co. Antrim, whilst the older felsitic rhyolites are abundant in Shropshire, North Wales, Lake District, and Scotland. They are used locally for building stones, especially on the continent (*e.g.* in Cologne Cathedral), and for millstones. The felsitic rhyolites being hard and tough are specially suitable for road-stones. L. J. S.

RICE, *Oryza sativa* (Linn.). A swamp grass which has been cultivated in Asia from remote ages. It is now extensively grown in Japan, China, India, the West Indies, Central America and the Southern United States. It forms the staple food of a very large proportion of the human race, but is chiefly used in the tropics.

[1] The Pharmaceutical Journal and Pharmacist, Sept. 1st, 1923, p. 276.

Many varieties are known, some of which have been claimed as distinct species, *e.g.* *O. montana*, growing in dry soils at altitudes up to 6500 ft.; *O. glutinosa*, or viscous rice, and *O. præcox*, or quick-growing rice, which matures in about 3 months, as against 5 or 6 months required by other kinds. The grain with its adhering husk is known as 'paddy,' but the rice imported into this country has had its outer brown husk removed.

According to König, the average weight of 100 grains of the three chief varieties is

	Viscous rice	Marsh rice	Hill rice
Unhusked	2·672	2·560	2·209 grms.
Husked	2·188	2·189	1·908 ,,

while the composition of the rice with husk is—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Viscous rice	12·6	5·1	3·0	73·4	4·5	1·3
Marsh rice	12·6	6·1	2·0	74·1	4·0	1·2
Hill rice	12·6	7·7	2·3	74·8	1·7	1·0

In various samples the protein varies from 5 to 10·5 p.c.; the starch from 72 to 80 p.c.

The rice deprived of its husk contains—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Japanese	11·1	8·5	1·9	76·0	1·0	1·5
East Indian	13·0	7·9	0·8	76·8	0·6	0·9
American	12·2	7·8	0·4	78·9	0·3	0·5

According to Wiley (Bull. 13 (1898) U.S. Dept. of Agriculture, 1182), the following figures represent typical samples:—

	Wt. of 100 grms. (grms.)	Water	Protein	Fat	Sol. carbohydrates	Crude fibre	Ash
Unhulled	3·00	10·5	7·5	1·6	67·4	9·0	4·0
Hulled	2·50	12·0	8·0	2·0	76·0	1·0	1·0
Hulled and polished	2·20	12·4	7·5	0·4	78·8	0·4	0·5

A large number of samples from Burmah, Carolina, India, Japan, Java, Piedmont, and Cochin China, examined by Balland (Compt. rend. 1895, 121, 561), yielded the following figures:—

	Water	Protein	Fat	Starch, etc.	Crude fibre	Ash
Crude, Max.	13·3	9·1	2·5	75·6	2·4	2·2
,, Min.	11·2	6·2	1·9	73·8	0·9	1·2
Decorticated, Max.	16·0	8·8	0·7	81·4	0·4	0·6
,, Min.	10·2	5·5	0·2	75·6	0·2	0·4

Balland found the acidity to lie between 0·03 and 0·06 in the refined rice, between 0·04 and 0·09 in the crude rice, while the sugars were 0·15 to 0·50 in the former and from 0·56 to 0·90 in the latter. Decortication greatly reduces the fat, nitrogenous matter, and ash, while polishing still further diminishes these constituents.

The proteids of rice (7 p.c.) contain a glutenin, *oryzenin*, soluble only in dilute alkali, about 0·14 p.c. of a globulin and 0·04 p.c. of an albumin (Rosenheim and Kajiura, Proc. physiol. Soc. 1908, 54). According to Suzuki, Yoshimura, and Fuji (J. Coll. Agric. Tokyo, 1909, 1, 77) the dry matter of rice, freed from husks, contained total nitrogen 1·200 p.c., of which 1·165 p.c. existed as true proteids. The cleavage products of the proteids were examined and estimated. They consisted largely of glutamic acid, 14·5 p.c.; leucine, 14·3 p.c.; alanine, 3·7 p.c.; proline, 3·3 p.c.; arginine, 1·6 p.c.; phenylalanine, 2·0 p.c.; ammonia, 2·33 p.c., with smaller quantities of

lysine, histidine, and tyrosine. *See also* Kurosawa (J. Tokyo, Chem. Soc. 1919, 40, 551).

Rosenheim and Kajiura attribute the unsuitability of rice for making dough and bread to the almost complete absence of an alcohol-soluble protein (gliadin). The prolonged use of an exclusive shelled-rice diet tends to the outbreak of the disease beri-beri; but this tendency can be destroyed by the addition to the diet of barley meal. They suggest that the increased supply of glutamic acid in hordein (from 35 to 41 p.c.) may partly explain this. The addition of rice-husks or of an alcoholic extract of rice-husks has a curative effect upon men or animals suffering from beri-beri (Kondô and Gomi, J. Pharm. Chim. 1915, 11, 37). *See also* Funk (J. Physiol. 1914, 48, 228); McCollum and Davis (J. Biol. Chem. 1915, 23, 181). For the vitamine content of rice, see Fleming (J. Biol. Chem. 1921, 49, 119).

The oil of rice was examined by Browne (J. Amer. Chem. Soc. 1903, 25, 948), who found indications of the presence of a fat-splitting enzyme in rice bran, to which he attributes the high proportion of free fatty acids, often found in oil from old rice. The germ and gluten layer of rice were found to contain about 15 p.c. of oil of sp.gr. $\frac{99°}{99°}$ 0·8907, m.p. 24°, acid value, 166·2; saponification value, 93·5; iodine value, 91·6; Reichert-Meissl value, 1·1; mol. equiv. of insoluble fatty acids 289·3, and m.p. of insoluble fatty acids 36°. According to Weinhagen (Zeitsch. physiol. Chem. 1917, 100, 159) rice bran contains 10·94 p.c. of fat. This can be separated into a liquid oil 73 p.c. and a solid fat (27 p.c.). The liquid contains 5·3 p.c. of phytosterol and 91 p.c. of fatty acids, 59 p.c. of oleic acid and 32 p.c. of palmitic acid. The solid portion contains 4·7 p.c. of phytosterol and about 91 p.c. of palmitic acid. A small quantity of a hydrocarbon, $C_{27}H_{48}$, m.p. 80°, is also present.

The ash of rice is rich in phosphoric acid and potash; analyses of the ash of Japanese rice by Kellner and Sawano (Landw. Versuchs.-Stat. 1884, 30, 18) gave the following figures:—

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_3	Cl
Marsh rice	22·9	4·9	3·2	10·5	1·0	51·4	1·9	3·1	1·0
Hill rice .	21·7	1·6	2·1	6·6	1·7	52·0	2·1	9·6	4·5

Rough rice, as produced by the planter, when sent to the mills, yields about 18 p.c. chaff and waste, 18 p.c. rice bran, 5 p.c. 'rice polish,' and 59 p.c. of clean rice.

Rice straw has some value as a fodder. Analyses of straw (1) from a good harvest and (2) from a poor harvest were made by Takeuchi (Bull. Coll. Agr. Tokyo, 1908, 7, 619)—

	Dry amtter	N	Fat	Dex-trose	Suc-rose	Starch	Pento-sans	Fibre	SiO_2
1 .	87·69	0·97	1·36	2·25	0·79	14·86	14·28	31·16	5·39
2 .	90·15	1·48	1·65	3·28	0·96	18·75	16·55	28·72	6·13

Rice bran and rice polish are valued as cattle foods. 'Rice meal' or 'rice feeding meal' consists of ground rice bran or a mixture of the bran and 'polish,' or sometimes largely of much less valuable ground chaff. Both bran and polish are rich in oil and albuminoids.

The following are analyses of various milling products of rice:—

	Water	Pro-tein	Fat	N-free extract	Crude fibre	Ash
Husks . .	10·0	3·7	1·4	32·3	38·1	14·5
Bran (Rangoon)	9·1	13·3	15·5	47·0	6·2	10·1
Polish . .	9·5	11·6	10·1	63·9	0·6	4·5

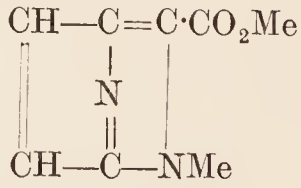
For the composition of rice polishings, *see* Drummond and Funk (Bio-Chem. J. 1914, 8, 598); Issoglio (Atti R. Accad. Sci. Torino, 1918–1919, 54, 440); Hofmeister (Biochem. Zeitsch. 1920, 103, 218).

For results of analyses of 159 samples of various Indian rice, *v.* Hooper (Agric. Ledger, 1908–1909, 5, 63).

Rice is used in the production of an alcoholic beverage, *sakè*, in Japan, and in the preparation of starch. The starch granules of rice resemble those of the oat, but are smaller (the average diameter of the simple grains being about 5μ, whilst those of the oat are about 10μ) and more angular. Compound grains made up of aggregations of the simple grains occur in the seed, but are very readily broken up on treatment with water, and occur very rarely in commercial rice starch. H. I.

RICINELAIDIC ACID, RICINOLEIC ACID *v.* Oils, Fixed, and Fats.

RICININE $C_8H_8O_2N_2$ occurs in castor oil seeds (of *Ricinus communis* [Linn.]) to the extent of 0·15 p.c., together with the toxalbumin 'ricin.' It crystallises from water or alcohol in rectangular prisms or tablets, m.p. 201°, sublimes without decomposition and is optically inactive. It is precipitated by mercuric chloride or iodine solution, but not by the usual alkaloidal reagents. Ricinine is sparingly soluble in cold water, readily in hot; the solutions are neutral and slightly bitter. It is apparently present in much larger proportion in the cotyledons of etiolated *Ricinus* seedlings (Evans, J. Amer. Chem. Soc. 1900, 22, 39). On hydrolysis with alkalis it yields methyl alcohol and *ricininic acid* $C_7H_6O_2N_2$, forming slender needles, decomposing at 150°. Maquenne and Philippe (Compt. rend. 1904, 138, 506; 139, 840) assigned an improbable formula to ricinine, but Böttcher (Ber. 1918, 51, 673, where are full references to the literature) have given evidence for a much more likely one (annexed), according to which it is the methyl ester of an N-methyldihydropyridine carboxylic acid, with a bridge of one nitrogen atom which makes it at the same time a glyoxaline



derivative, like pilocarpine. *Cf.* Späth and Tschelnitz, Monatsh. 1921, 42, 251; Späth and Koller, Ber. 1923, 56, 880, 2454. For a method of preparing ricinine, *see* Winterstein, Keller, and Weinhagen, Arch. Pharm 1917, 255, 513; J. Soc. Chem. Chem. Ind. 1919, 738 A. For the synthesis of ricinine, *see* E. Späth & G. Koller (Ber. 1923, 56, 2454; J. Soc. Chem. Ind. 1924, 43, B 151). G. B.

RICINUS OIL *v.* Castor oil; also Oils, Fixed, and Fats.

RICKARDITE. Copper telluride, Cu_4Te_3, known only as a massive mineral. On fresh fractures it shows a characteristic rich purple colour resembling an iridescent tarnish; but on exposure to light it becomes changed on the surface to a dull brown powder. Sp.gr. 7·54; H.=3½; soluble in nitric acid. It is found associated with native tellurium, petzite, &c., in a pyrites vein at Vulcan in Colorado, and intricately veined with free gold with gold tellurides at Kalgoorlie in Western Australia.

L. J. S.

RINKITE. Silicate (titanate, zirconate, and fluoride) of cerium metals (Ce_2O_3, &c, 21·2–23·3 p.c.), calcium, and sodium,

$$Ce_2Ca_4Na_3(Si,Ti)_6O_{19}F_3$$

crystallised in the monoclinic system with a square tabular habit. The colour is straw-yellow; sp.gr. 3·46, H.=5. The mineral fuses readily before the blowpipe with intumescence to a black shining glass; and it is easily decomposed by dilute acids with separation of silica. It appears to be of not infrequent occurrence in nepheline-syenites, *e.g.* at Kangerdluarsuk in Greenland, Serra de Tingua in Brazil, the Los Islands off the West Coast of Africa, and in the Pyrenees; it has also been detected in phonolite from the Auvergne. L. J. S.

RINMANN'S GREEN *v.* Cobalt.

RINNEITE. Anhydrous chloride of ferrous iron, potassium (K 28·7 p.c.), and sodium, $FeCl_2{\cdot}3KCl{\cdot}NaCl$, crystallised in the rhombohedral system. It forms coarsely granular masses with perfect cleavages parallel to the faces of the hexagonal prism. When pure and fresh it is colourless, rose-pink, violet, or yellowish, but on exposure to the air it quickly becomes brown. Specimens may be preserved in petroleum. Sp.gr. 2·35; H.=3. The mineral is found in considerable quantity, forming large lenticular masses in beds of rock-salt, sylvite, and anhydrite at Wolkramshausen near Nordhausen in the Harz. At Diekholzen near Hildesheim and at Salzdetfurth and Riedel in Hanover it forms a kieserite-rinneite rock. The triple salt can be prepared artificially at temperatures between 26·4° and 38°. L. J. S.

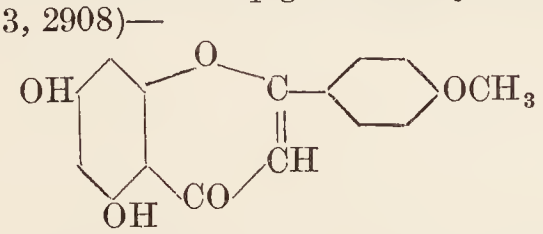
RIONITE. A bismuth fahlore found at Cremenz, in the Canton Wallis.

RISÖRITE. Columbate (and titanate) of yttrium, $(Y,Er)_2O_3$ 36·28 p.c., forming yellowish-brown masses with conchoidal fracture and resinous lustre. Sp.gr. 4·18; H.=5½; optically isotropic; soluble in hot concentrated sulphuric acid. It is found in granite-pegmatite at Risör in the south of Norway. L. J. S.

ROBINIA PSEUDACACIA. *Acacetin*, $C_{16}H_{12}O_5$, the colouring matter of the leaves of the *Robinia pseudacacia* (Linn.) (common or false acacia, North American locust), forms almost colourless needles, soluble in alkalis with a pale yellow coloration (Perkin, Chem. Soc. Trans. 1900, 71, 430).

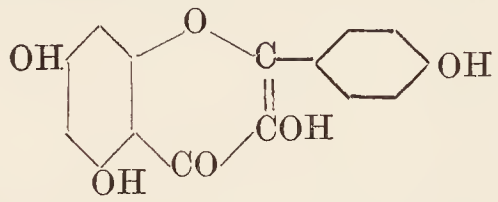
To prepare it a boiling aqueous decoction of the leaves is treated with basic lead acetate solution, and the pale yellow precipitate is suspended in water and decomposed with boiling dilute sulphuric acid. From the clear liquid the colouring matter is removed by extraction with ether and purified by crystallisation from dilute alcohol.

Acacetin forms a *diacetyl derivative*, $C_{16}H_{10}O_5(C_2H_3O)_2$, colourless needles, m.p. 195°–198°, and when fused with alkali gives phloroglucinol and *p*-hydroxybenzoic acid. Digested with boiling hydriodic acid it yields apigenin and one molecular proportion of methyl iodide, and is consequently an *apigenin monomethylether*. Acacetin is very probably identical with von Gerichten's apigenin methyl ether (Ber. 1900, 33, 2908)—



the acetyl derivative of which melts at 198°–200°.

Interesting is the fact that the flowers of the *Robinia pseudacacia* contain *robinin*, a glucoside of the trihydroxy flavonol, kaempferol—



which contains one more hydroxyl than apigenin. Robinin was first isolated from the flowers of the white azalea by Zwenger and Dronke (Annalen, Supp. 1861, 1, 263), who considered that it was a glucoside of quercetin. Perkin (Chem. Soc. Trans. 1902, 81, 473) has shown that this is not the case.

To prepare the glucoside the flowers are exhausted with boiling alcohol, the solution concentrated by evaporation and poured into water. The mixture is extracted with ether, and the aqueous liquid distilled down to a small bulk. On standing, crystals of robinin separate, which are purified by crystallisation from water.

Robinin, according to Perkin, consists of pale yellow needles, sintering at 190° and melting at 196°–197°, and when air-dried it possesses the formula $C_{33}H_{42}O_{20},8H_2O$.

Boiling dilute sulphuric acid hydrolyses robinin with formation of kaempferol, 2 molecular proportions of rhamnose and 1 of glucose, according to the following equation:—

$$C_{33}H_{42}O_{20}+4H_2O = C_{15}H_{10}O_6+2C_6H_{14}O_6+C_6H_{12}O_6$$

Schmidt (Chem. Zentr. 1901, [ii.] 121), who examined robinin at almost the same time, also obtained by its hydrolysis a colouring matter $C_{15}H_{10}O_6$, the acetyl compound of which melts at 182°–183° (evidently kaempferol), and Waliaschko (J. Russ. Phys. Chem. Soc. 1904, 36, 421), again, no doubt, also unaware of the communication of Perkin, terms this colouring matter $C_{15}H_{10}O_6,H_2O$, *robigenin*. Robinin he considered to possess the formula

$$C_{33}H_{40}O_{19}{\cdot}7\tfrac{1}{2}H_2O$$

and the sugars that it yields by hydrolysis to consist of galactose (1 mol.) and rhamnose (2 mols.).

Robinin is a most interesting glucoside, and with the exception of xanthorhamnin is the only known substance of this class which yields three sugar nuclei. It is practically devoid of tinctorial property.

Interesting is the fact that whereas the bark of this plant contains *acacetin*, the monomethyl

ether of the trihydroxyflavone, apigenin, its flowers yield the glucoside of the trihydroxyflavonol, kaempferol. Whether the occurrence of distinct flavones in various portions of the same plant is exceptional or otherwise, has been little studied, and appears to have only been observed elsewhere in the cases of the yellow cedar (*Rhodesphacra rhodanthema*), the leaves of which contain quercetin and the stem fisetin, and the Venetian sumach, the stem of which contains fisetin and the leaves myricetin.

According to Tasaki and Tanaka (J. Coll. Agric. Tokyo, 1918, 3, 337) the bark of *Robinia pseudacacia* contains about 3 p.c. of a glucoside, *robitin*, which causes toxic symptoms in horses and cattle. It is a white hygroscopic, amorphous powder, soluble in water and acids, and on hydrolysis yields dextrose and rhamnose (*cf.* Power, Pharm. Rundschau, 1890, 8, 29; Pharm. J. 1901, 67, 258; Amer. J. Pharm. 1913, 339; Holmes, Pharm. J. 7, 1923, 110, 263). A. G. P.

ROBININ *v.* Glucosides and Robinia.

ROBITIN *v.* Robinia.

ROBURITE *v.* Explosives.

ROCCELLA *v.* Archil and Lichens.

ROCCELLIN *v.* Azo- colouring matters.

ROCELLIC ACID $C_{15}H_{30}(CO_2H)_2$. Obtained from various lichens, from *Rocella fuciformis* and *R. tinctoria* (Hesse, J. pr. Chem. [ii.] 57, 261), *Lecanora sordida* (Hesse, *ibid.* 58, 497), *L. cenisea* and *Lepraria latebarum* (Zopf, Annalen, 295, 264, and 298); white silky plates, m.p. 127°–128°. The anhydride is an oil (*cf.* Schunck, Chem. Soc. Trans. 1848, 3. 153), *v.* Lichens.

ROCHELLE SALT *v.* Tartaric acid.

ROCK, ALUM. *Alunite v.* Alums.

ROCK-CRYSTAL *v.* Quartz.

ROCK OIL *v.* Petroleum.

ROCK-PHOSPHATE *v.* Phosphorite.

ROCK SALT *v.* Halite; Sodium chloride.

RODAGEN *v.* Synthetic drugs.

RODINAL. A solution of *p*-aminophenol, used as a photographic developer.

ROMAN ALUM *v.* Alums.

ROMAN CEMENT *v.* Cement.

ROMANECHITE *v.* Hollandite.

ROMAN LAKE. *Crimson lake v.* Pigments.

ROMAN OCHRE. A variety of argillaceous ferric oxide of an orange-yellow colour, used as a pigment.

ROMITE *v.* Explosives.

RONGALITE. Trade name for sodium formaldehyde sulphoxylate.

ROSANILINE and **ROSANILINE DYES** *v.* Triphenylmethane colouring matters.

For rosaniline-sulphurous acid and its colour reactions with aldehyde, *see* Wieland and Scheuing (Ber. 1921, 54, (B), 2527–2555).

ROSCOELITE or Vanadium-mica. A member of the mica group of minerals (*q.v.*) similar to muscovite in composition but with alumina largely replaced by vanadous oxide (V_2O_3 reaching 28·85 p.c.). It occurs in some abundance as sage-green scaly masses, intimately associated with native gold and gold tellurides, in Eldorado Co. in California, in the Magnolia and Cripple Creek districts in Colorado, and at Kalgoorlie in Western Australia. In larger quantities it occurs, together with carnotite (*q.v.*), as an impregnation in Jurassic sandstone near Placerville in San Miguel Co., Colorado. The roscoelite forms up to 20 p.c. of the mass of the sandstone in a bed varying from a few inches to 5 or 6 ft. in thickness. Attempts have been made at Newmire, Colorado, to utilise this roscoelite-bearing sandstone as a source of vanadium. Analyses by W. F. Hillebrand (Amer. J. Sci. 1899, 7, 451; 1900, 10, 120): I, from Granite Creek, Eldorado Co., California; II, from Placerville, Colorado.

	I.	II.
SiO_2	45·17	46·06
TiO_2	0·78	—
V_2O_3	24·01	12·84
Al_2O_3	11·54	22·55
Fe_2O_3	—	0·73
FeO	1·60	—
CaO	—	0·44
BaO	—	1·35
MgO	1·64	0·92
K_2O	10·37	8·84
Na_2O	0·06	0·22
H_2O (105°)	0·40	1·98
H_2O (>105°)	4·29	4·07
	99·86	100·00

L. J. S.

ROSE. The colouring matter of the red rose is due to the anthocyanin pigment cyanin, which is present to the extent of 10 p.c. in the dried petals of the deep red rose 'George Dickson' (Currey, Proc. Roy. Soc. 1922, B, 93, 194).

For Indian Otto of Rose, *see* J. Soc. Chem. Ind. 1922, 41, 192 R.

ROSE ATTAR *v.* Oils, Essential.

ROSEÏNE. A synonym for fuchsine or aniline-red: *v.* Triphenylmethane colouring matters.

ROSELLE. The edible calyx of the roselle plant (*Hibiscus sabdariffa*, L.) is used in making jam or jelly of a brilliant red colour and pleasant acid taste, due to dextro-rotatory malic acid. Analysis by Pratt (Philippine J. Science, 1912, 7, 201; Analyst, 1912, 60).

Water	Solids	Ash	Marc	Malic acid	Invert sugar	Sucrose
82·49	17·51	1·26	7·39	3·31	0·82	0·24

ROSEMARY OIL *v.* Oils, Essential.

ROSENTHIEL'S GREEN or **CASSEL GREEN.** *Barium manganate.* It is also known as *manganese green.* It is a very unstable pigment.

ROSE OIL *v.* Oils, Essential.

ROSE PINK. A pigment prepared by dyeing whiting with Brazil wood. It is too fugitive for artistic use, but is much employed in paper-staining.

ROSEWOOD, OIL OF. A volatile oil obtained from the wood of *Convolvulus scoparius* by distilling with water. A light-yellow oil consisting mainly of a terpene $C_{10}H_{16}$; b.p. 249°. Used occasionally for adulterating oil of roses, *v.* Oils, Essential.

ROSHYDRAZINE. The colour and leucobases of triphenylmethane, when diazotised and treated with $SnCl_2$, are readily converted into hydrazines. For example: Rosaniline (5 grms.) is dissolved in 30 c.c. of hydrochloric acid and 70 c.c. of water, and the iced solution is diazotised by adding 3½ grms. $NaNO_2$ in 10 c.c. of water. On mixing the solution of the diazo-compound with a well-cooled solution of 12 grms. of tin in 30 c.c. of hydrochloric acid, the *roshydrazine hydrochloride* separates in green, shimmering crystals. The salt is easily soluble

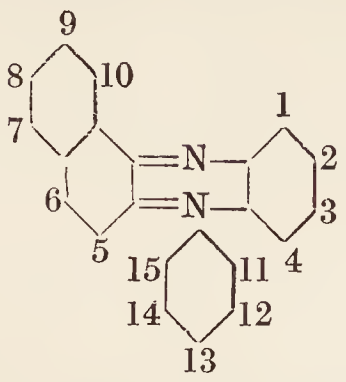
in water, nearly insoluble in hydrochloric acid. Its solution has a bluer shade than rosaniline; it is a strong colouring matter, and dyes tannined cotton a deep brownish-red. Like other hydrazines, it reduces Fehling's solution, and forms condensation products with aldehydes and ketones. The latter compounds are sparingly soluble dyestuffs; thus acetone, aldehyde, pyruvic acid, benzophenone, &c., give reddish to bluish-violet colours; acetoacetic ester and benzaldehyde give blues; whilst glucose gives a greyish-blue. Benzaldehyde sulphonic acid yields a blue soluble in water. These condensation products can also be formed upon the fibre. The reduction of the diazo-compound of acid-magenta gives rise to easily-soluble sulphonic acids of roshydrazine, the condensation products of which are soluble colouring matters. Safranine, when treated in the same way, does not give a hydrazine, but evolves nitrogen (J. H. Ziegler, Ber. 1887, 20, 1557; J. Soc. Chem. Ind. 6, 594).

ROSIN OIL, ROSIN SPIRIT *v.* RESIN OIL.

ROSINDULINE $NH{:}C_{10}H_5{\leqslant}^{N}_{NPh}{>}C_6H_4$ is prepared by heating benzeneazo-α-naphthylamine hydrochloride (1 part) with aniline (2 parts) and alcohol (4 parts) under pressure at 160°–170° for 6–8 hours. The alcohol is then evaporated and the excess of aniline is distilled off with steam. The residue is filtered and then extracted several times with boiling water. The combined filtrates are allowed to stand for a few days, then decanted from the resinous products, the solution acidified with hydrochloric acid and precipitated with sodium chloride, when the hydrochloride separates in long red needles, from which the base may be obtained by decomposing with soda and extracting with ether (Fischer and Hepp, Annalen, 1890, 256, 233; D. R. P. 71296). It may also be obtained by passing a stream of air through, and warming an alcoholic solution of phenylnaphthaphenazonium sulphonic acid to which ammonia has been added (Kehrmann and Locher, Ber. 1898, 31, 2430; Kehrmann and Schaposchnikoff, *ibid.* 1897, 30, 2627). For other methods of preparation, see Kehrmann and Messinger, *ibid.* 1891, 24, 587, 2167; Fischer and Hepp, *ibid.* 1896, 29, 2760; Annalen, 1895, 286, 227; Kehrmann, *ibid.* 1896, 290, 268).

Rosinduline forms reddish-brown plates, m.p. 198°–199°, readily soluble in ether, benzene or alcohol; insoluble in water: readily absorbs carbon dioxide from the air and is decomposed by concentrated hydrochloric acid forming ammonia and rosindone. It forms salts with the mineral acids, and yields the *hydrate* $C_{22}H_{15}N_3,H_2O$, m.p. 185°–187°. When the base is diazotised in strong acid solution, and then treated with alcohol, it forms naphthaphenazonium. Unlike *iso*rosinduline, it does not combine with tetramethyldiaminobenzhydrol. According to Kehrmann (Ber. 1894, 27, 3348; *ibid.* 1896, 29, 2316, 2967; Annalen, 1896, 290, 247), rosindulines are *o*-quinoidal azonium compounds, but Fischer and Hepp regard them as derivatives of αβ-naphthaphenazine (Annalen, 1892, 272, 306; Ber. 1896, 29, 361, 2752).

The effect of introducing the amino group into rosinduline in different positions has been studied by Kehrmann, Rademacher and Feder (Ber. 1898, 31, 3076), who have found that representing the scheme of numbering thus,



the introduction of an amino group into the para position (2) with respect to the azonium nitrogen gives a bluish-violet dyestuff with scarcely any fluorescence. On the other hand, an amino group at 13 or in any position of this phenyl group causes hardly any increase in the depth of shade, the diamine 6 : 13, scarcely differing in colour from rosinduline which has an amino group at 6, whilst the triamines, 2 : 6 : 13, 2 : 6 : 12, are bluish-violet and differ little from the diamine 2 : 6. The introduction of an amino group para to the azine nitrogen at 3 causes little alteration in shade, but increases the tinctorial value of the colour and the fluorescence. These facts are analogous to those known for the safranines of the benzene series.

A number of nitro- and amino-rosinduline chlorides have been prepared (*see* also Kehrmann, Chem. Zentr. 1900, ii. 813).

Ethylrosinduline may be obtained in the same way as rosinduline by using benzeneazo-α-ethyl naphthylamine. It has m.p. 184°, gives a green solution in sulphuric acid, which turns red on addition of water and like rosinduline it is a good dye.

Methylrosinduline is obtained by boiling the anhydride of phenylnaphthaphenazonium sulphonic acid with methylamine in alcohol (Kehrmann and Locher, *l.c.*). It forms gold coloured leaflets, m.p. 180°–181°, and behaves like the ethyl derivative with sulphuric acid.

Phenylrosinduline may be prepared by heating 5·8 grms. *p*-nitrobenzeneazo-α-naphthylamine with 15 grms. of aniline at 160°–165° for 2 hours (Paul, Chem. Zentr. 1897, i. 1168); by heating α-nitronaphthalene with aniline and aniline salts (D. R. PP. 67339, 45370) and by many other methods (Kehrmann and Locher, *l.c.*; Fischer and Hepp, Ber. 1888, 21, 2621; 1897, 30, 1829; Annalen, 1890 256, 233). It forms dark-red needles, m.p. 234°, almost insoluble in water and sparingly soluble in organic solvents. Its neutral salts are red, whilst the acid salts are green, the dyeing properties of the hydrochloride being analogous to the fuchsine dyes. With concentrated sulphuric acid it forms an almost insoluble *monosulphonic acid*, whilst with fuming sulphuric acid it gives a *di-sulphonic acid* known as *azocarmine*; a trisulphonic acid readily soluble in water known as *rosinduline 2B* has also been obtained (D. R. PP. 52922, 79953, 59180, 64993, 67198, 72343; Eng. Pat. 8184, 1894).

Hydroxyphenylrosindulines, from which sulphide dyes have been prepared, are obtained by heating *p*-amino-*o*-cresol with benzeneazo-α-naphthylamine in water or alcohol (D. R. P. 158077; J. Soc. Chem. Ind. 1906, 175).

Trihydroxyphenylrosinduline may be pre-

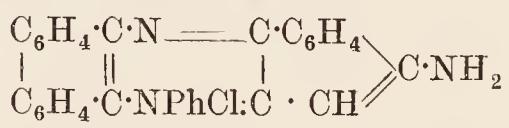
pared from substances such as the dyestuffs obtained by combining diazo- compounds with α-naphthylamine by heating with *p*-amino phenol and hydrochloric acid or by treating 1 : 4 naphthalene diamine similarly and oxidising the product with an aromatic nitro- compound : also by heating α-nitronaphthalene with *p* aminophenol and hydrochloric acid (D. R. PP. 158077, 158100, 160789).

When benzeneazomonoaryl -α- naphthylamines or monoaryl-1 : 4-diaminonaphthalene replaces the benzeneazo-α-naphthylamine, the resulting dyestuffs are said to produce purer and bluer shades (D. R. P. 160815).

Halogen and other derivatives of phenylrosinduline have been prepared, many of which are also used in dyeing.

o-*Tolylrosinduline* can be obtained by heating rosindone with *o*-toluidine and its hydrochloride at 150°–170° (D. R. PP. 15894, 67115). It forms readily soluble sulphonic acids with fuming sulphuric acid : p-*tolylrosinduline* (D. R. P. 65894 ; Fischer and Hepp, *l.c.*), *naphthylrosinduline* (D. R. P. 71296 ; Fischer and Hepp, *l.c.*), have also been prepared.

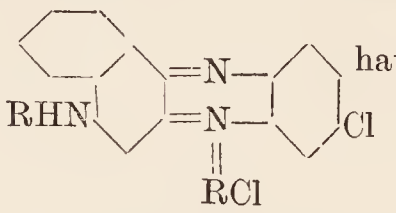
Phenanthrarosinduline



is prepared by the action of ammonia and air on naphthaflavinduline chloride. It crystallises in dark red prisms with a bronze-like lustre (Kehrmann and Eichler, Ber. 1901, 34, 1210).

Phenylphenanthrarosinduline is prepared by the action of aniline on naphthaflavinduline and forms large dark violet crystals with a copper-like lustre (Kehrmann and Eichler, *l.c.*).

Chloro- substituted rosindulines of general formula



have been formed by condensing chloro- derivatives of substituted *o*-diamines of the general formula

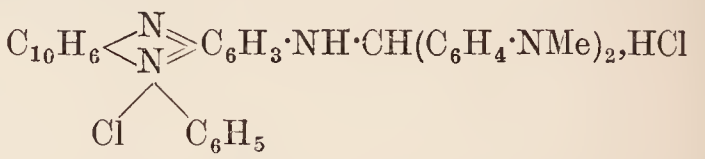
$$C_6H_3Cl(NH_2)NHR(1:4:2)$$

(R=aromatic or aliphatic radicle) with 4-amino and 4-anilino β-naphthaquinone. These dyestuffs give blue shades and when treated with amines are converted into safranine dye-stuffs (Eng. Pat. 14238, 1899 ; J. Soc. Chem. Ind. 1900, 530).

iso-*Rosindulines*. This name was originally applied to the rosindulines having the NH group in the phenyl portion of the molecule and the 3-NH derivative, $C_{10}H_6N{\cdot}NPh{\cdot}C_6H_3NH$ (see above), was first prepared by Nietzki and Otto (Ber. 1888, 21, 1601) by warming an alcoholic solution of phenyl-β-naphthylamine (1 mol.) with quinonedichlorimide. It is a bluish-violet powder forming violet solutions in alcohol and ether.

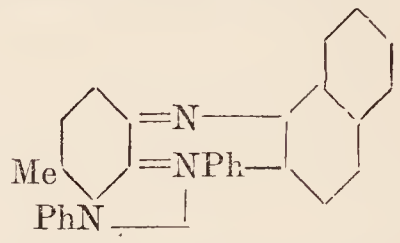
*Phenyl*iso*rosinduline* is obtained by the action of nitrosodiphenylamine and phenyl-β-naphthylamine (Fischer and Hepp, Ber. 1896, 29, 2753) or by allowing an alcoholic solution of chlorophenylnaphthazonium chloride and aniline to stand for several hours (*ibid.* 1898, 31, 304 ; *ibid.* 1900, 33, 1496). It forms copper-coloured crystals, m.p. 169°–171°, gives a blue solution in benzene and alcohol and is converted into *iso*rosindone when heated with glacial acetic and hydrochloric acids at 235°.

*Iso*rosinduline chloride reacts with tretamethyldiaminodiphenylbenzhydrol, forming a leucauramine,



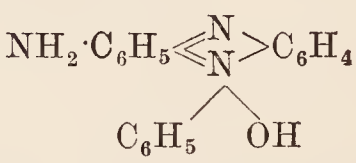
from which dyestuffs can be obtained giving red yellow shades on cotton mordanted with tannin (Mohlau and Schaposchnikoff, Ber. 1900, 33, 799).

β-*o*-*Methylphenyl*iso*rosinduline*



may be obtained by boiling an alcoholic solution of β-*o*-methylchlorophenylnaphthaphenazonium chloride with 2 molecular proportions of aniline for several hours. It forms coppery crystals which give a blue solution in sulphuric acid. The corresponding tolyl rosinduline, m.p. 226°, and the β-naphthyl compound, which is a reddish-violet dyestuff, are prepared similarly (Fischer, Ber. 1901, 34, 940).

Kehrmann has, however, applied the term *iso*rosinduline to the base



the NH_2 group occupying any one of the 15 positions in the naphthyl, or either of the phenyl groups, and he has prepared 15 such chloro-derivatives of *iso*rosinduline (aminophenylisonaphthaphenazonium chlorides), of which two or three may be mentioned as examples. Their numbers refers to the order in which they were prepared, not to the position of the NH_2 group.

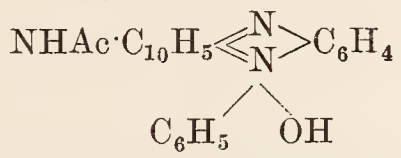
iso-*Rosinduline*, *No.* 5 (2-aminophenylnaphthaphenazonium chloride), exists in two modifications. The labile form is obtained by reducing 2 - nitrophenylnaphthaphenazonium chloride with tin chloride and hydrochloric acid at 0°. It gives reddish-violet solutions in alcohol and in water. On addition of dimethylamine to the former solution it turns green, then passes into blue and finally becomes fuchsine red. The stable form is prepared by carrying out the above reduction without any artificial cooling. It forms a dirty violet aqueous solution and a blue alcoholic solution which becomes fuchsine red on addition of dimethylamine (Kehrmann and Valencien, Ber. 1900, 33, 409).

iso-*Rosinduline*, *No.* 12, the 8 amino-derivative is obtained thus : phenyl*iso*naphthaphenazonium nitrate is treated with conc. nitric acid, and the two-mononitro derivatives thus obtained are extracted with alcohol, precipitated with ether and reduced with tin chloride and hydrochloric acid. The tin double compound is oxidised in alcoholic solution with ferric chloride, the precipitate dissolved in water, treated with sodium acetate and then with sodium bromide.

The bromide of No. 10 *iso*rosinduline is removed by solution in a little hot water and a saturated solution of sodium bromide is then added, when the bromide of No. 12 separates as steely almost black prisms sparingly soluble in cold, readily so in hot water and giving a brown-red solution in sulphuric acid which turns orange-yellow on dilution and dirty greenish-blue on neutralisation (Kehrmann and Steiner, Ber. 1900, 33, 3276).

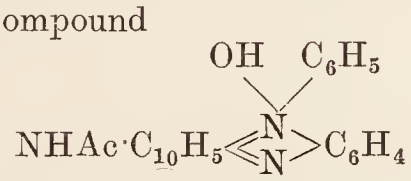
iso-*Rosinduline*, *No.* 15 (12-aminophenylnaphthazonium chloride) is formed by the interaction of 4 : 1 : 2-aminonaphthaquinone and 2 : 3′diaminodiphenylamine in the presence of a drop of dilute hydrochloric acid. The product is converted into the diacetyl derivative which, on boiling with hydrochloric acid in alcoholic solution, yields 6 : 12-diaminophenylnaphthaphenazonium chloride. The latter is converted into the acetyl derivative, diazotised, treated with sodium bromide and then hydrolysed with sulphuric acid when the desired compound separates in dark, yellow-brown greenish metallic granules, sparingly soluble in water and giving a violet solution in sulphuric acid. The solutions are non-fluorescent and have a bitter taste (Kehrmann and Nüesch, Ber. 1901, 34, 3099). The dichromate forms lustrous golden-yellow laminæ.

*Acetyl*iso*rosinduline* exists in two modifications : the α-compound



forms red needles, with a green metallic lustre, which decompose at 290°. It forms a yellowish-red fluorescent solution in alcohol and when boiled with hydrochloric acid it yields rosinduline salts.

The β-compound



forms dark brown-red plates with a metallic lustre which decompose at 260°, more readily soluble in alcohol than the α-compound, the solutions being dark red and non-fluorescent. When boiled with hydrochloric acid it yields an *iso*rosinduline salt (Kehrmann and Hertz, Annalen, 1896, 290, 262 ; Kehrmann and Aebi, Ber. 1899, 32, 932).

For the other *iso*rosindulines, see Kehrmann and Ravinson (Ber. 1899, 32, 927) ; K. and Filatoff (*ibid.* 2627) ; K. and Levy (*ibid.* 1898, 31, 309) ; K. and Denk (*ibid.* 1900, 33, 3295) ; K. and Wolff (*ibid.* 1543) ; K. and Silberstein, 3300) ; K. and Misslin (*ibid.* 1901, 34, 1224) ; K. and Ott (*ibid.* 3092).

For other literature on rosinduline and *iso*rosinduline and their derivatives, *v.* Fischer and Hepp (Annalen, 1890, 262, 237 ; Ber. 1900, 33, 1485) ; Kehrmann and Schaposchnikoff (*ibid.* 1896, 29, 2967 ; *ibid.* 1897, 30, 1565) ; Schraube and Romig (*ibid.* 1893, 26, 575) ; Kehrmann and Hiby (*ibid.* 1901, 31, 1085) ; Kehrmann and Silberstein (*ibid.* 1900, 33, 3280, 3285). Also the references already given.

ROSINS *v.* Resins.

ROSOCYANIN *v.* Turmeric.

ROSOLIC ACID *v.* Triphenylmethane colouring matters.

ROSOPHENINE 10 B. *v.* Primuline and its derivatives.

ROTRA BARK *v.* Tannins.

ROTTENSTONE. A disintegrated rock which, when washed and ground, is used as a polishing material for metal, marble, &c. It is usually regarded as the residual matter left on the natural decompositions of impure limestone. If the limestone be silicious, the silica may be left in a very finely-divided condition ; but old analyses of Derbyshire rottenstone show a very large proportion of alumina. The rottenstone of Derbyshire occurs in irregular cavities in the carboniferous limestone, and the best kinds are said to be obtained from a black bituminous limestone near Ashford, and on Bakewell Moor. It has also been worked in South Wales, especially in the counties of Brecon, Carmarthen, and Glamorgan. The term ‘ rottenstone ’ is sometimes applied to *tripolite*, a material consisting of highly-comminated silica, which is mostly derived from the frustules or silicious cases of the unicellular algæ known as diatoms.

ROTTLERIN *v.* Resins.

ROUGE *v. Iron oxides*, art. Iron.

ROUILLE *v. Iron oxides*, art. Iron.

ROWLANDITE. Yttrium silicate containing Y_2O_3 47·7–61·9 p.c., with some cerium-earths, &c. It forms nodular masses with a resinous lustre and conchoidal fracture. These are pale drab-green when pure, but are generally altered to brown. The streak is greenish-grey ; thin splinters are transparent and optically isotropic. Sp.gr. 4·51 ; H.=6 ; easily soluble in acids with separation of gelatinous silica. The mineral occurs with gadolinite, &c., at Barringer Hill in Llano Co., Texas. L. J. S.

ROYAL BLUE. *Smalt v.* Cobalt ; also Pigments.

RUBBER (*India-rubber*, *Caoutchouc*) is a substance possessing peculiar and valuable physical, mechanical (tensile), and chemical properties, by virtue of which it is widely employed in numerous industries and arts and for many domestic purposes. The main constituent of the commercial article is a hydrocarbon possessing the empirical formula $(C_5H_8)n$ or $(C_{10}H_{16})n$. Rubber is generally derived by a process of coagulation from a fluid (*latex*) contained in a special cell system (*laticiferous system*) of various trees, creepers, and shrubs. It also occurs occasionally in the solid state, in the form of a deposit in the woody fibre of certain species, for instance in *Parthenium argentatum* (guayule). The laticiferous system, which is distinct from the sap-bearing cell system, generally lies between the outer bark and the cambium, and by cutting through the former and into the latex cells, the latex is obtained in the form of a white to cream coloured, more or less viscous fluid. This operation is termed ‘ tapping.’ The rubber is contained in the latex in the shape of small particles (varying according to species from roughly 0·5 to 4μ in diameter), which are generally suspended in the serum in the form of a negative emulsion. The rubber is separated from the latex either by evaporating a part of the water or by a process of coagulation which varies according to the species, district, &c. After the coagulum has been separated from the

Order	Genus	Species	Occurrence, etc.
Euphorbiaceæ .	Hevea	brasiliensis (Muell. Arg.)	*South America*, particularly *Brazil;* employed practically to exclusion of all other trees on Eastern plantations. Forms *Para* rubber of commerce.
,, .	Manihot	Glaziovii (Muell. Arg.); dichotoma	*Ceará* (*Brazil*); planted to some extent in Africa and tropical America. Forms the *Ceara* or *Manicoba* rubber of commerce.
,, .	Sapium	Tolimense; verum, &c.	*Central and South America* (*Colombia Virgen; Carthagena Scraps*, &c. of commerce).
Apocynaceæ .	Funtumia	elastica (Stapf)	*Tropical Africa;* forms *Gold Coast Lumps*, *Ivory Coast Lumps*, and various '*niggers*,' &c. of commerce. Planted in some parts of Africa.
,, .	Landolphia	owariensis (Beauv.); Heudelotii D.C. Thollonii (Dew.); sphærocarpa (Jumelle); Pierrei	Creepers occurring in enormous quantities in *Tropical Africa*, forming many of the 'Congo' varieties, '*Madagascars*,' &c. of commerce.
,, .	Clitandra	Numbers of species of this genus are distributed in many parts of *tropical Africa*, principally Gold Coast and Congo	
,, .	Hancornia	speciosa (Gomez) (Muell. Arg.)	*Brazil* (Bolivia and Pernambuco) yields the '*Mangabeira*,' *Bahia*, and *Matto-grosso sheets* of commerce.
,, .	Dyera	costulata (Hook. *f.*)	*Malay Peninsula;* yields '*Jelutong*' of commerce.
Urticaceæ .	Ficus	elastica (Roxb.)	*Asia* (Burmah, Malaya, Java, India). Yields the '*Rambong*' of commerce. Has been planted to some extent in the Dutch and late German colonies.
,, .	Castilloa	elastica (Cerv.); *Ulei* (Warb.)	*Mexico; Central America; Peru.* Planted to some extent in Mexico and late German colonies, &c. Yield the '*Caucho*,' '*Mexican strips*,' '*Centrals*,' &c. of commerce.
Compositæ .	Parthenium	argentatum (A. Gray)	*Mexico; Texas* (*Guayule* of commerce).

serum it is generally purified and dried to a greater or less extent, and is then exported in the form of balls, loaves (*fine Para*), sheets, crepe, block (plantation species), slabs, irregular lumps, 'sausages,' 'thimbles,' &c.

Rubber-bearing species.—The chief orders, genera, and species are shown on page 700.

Collection of latex and *coagulation.*—In the Amazon district from which the 'fine Para' brands of commerce are obtained, the methods employed are briefly as follows: The trees are tapped with a small axe (machadinha), the incisions taking the form, generally, of V cuts or oblique lines. The first tappings are made at a height of 6–7 ft., subsequent incisions at intervals of roughly 1½–2 ins. beneath the first one, until the base of the tree is reached. This process is then repeated, the next tapping line (arraçao) commencing at a horizontal distance of about 18 ins. from the first one. The latex is collected in small tin or earthenware cups fixed to the tree by means of moist clay. The daily yield of latex from a mature tree is stated to be about 1½ oz., which corresponds roughly to 5 lbs. of rubber per tree per season, but it is doubtful whether any large proportion of the forest trees show as high a yield as this over a succession of seasons. After the *seringueiro* (as the rubber worker is termed) has completed his tapping round, he covers the same ground again in order to collect the latex. From the cups the latter is transferred to pails, thence to flat basins, and is subsequently cured by a smoking process which is carried out in the following manner:—

In a small brazier a fire is made, consisting largely of material giving a dense smoke rich in the products of dry distillation of woody matter (creosote, tarry matter, acetic acid). For this purpose the fruit (nuts) of the *urucuri* palm (*Attalea excelsa* [Mart.]) are considered particularly suitable. A mandril, consisting of a long wooden rod or paddle is so disposed, one end on a cross piece, the other on the operator's knees, that it can be rolled either over the top of the chimney—and so be exposed to the full volume of smoke—or over the basin containing the latex. The operator then pours a small

quantity of latex over the wooden paddle or rod, thus forming a thin film of liquid. This is rotated in the smoke until it sets. A fresh quantity of latex is then poured on to the first film, smoke is again applied, and so on, until a biscuit or ball of rubber of the required size (20–100 lbs. is the general average weight) consisting of innumerable thin layers tightly adhering to one another, is formed. The ball is then removed from the mandril and is ready for export, forming the 'fine Para' of commerce.

'Up-river' (*i.e.* above Manaos) 'fine Para' is generally of the type termed *hard cure*, 'Islands' rubber (*i.e.* that from the mouth of the Amazon) generally as *soft cure*. The main difference is that indicated by the names. Imperfectly cured loaves are known as *entre-fine*. The scrappy rubber formed by premature coagulation on the tree or in the collecting or coagulating vessels is compressed (*unsmoked*) into irregular masses, and goes by the name of *Negro-heads*. Whereas the Amazon territory formerly supplied the bulk of the world's rubber, the production at the time of writing (1923) is about 30,000 tons out of a total of roughly 375,000 tons.

Plantation rubber.—The tree which has been almost universally adopted on the eastern plantations (Malaya, Ceylon, S. India, Java, Sumatra, Borneo) is the *Hevea brasiliensis*, but the methods of collection and coagulation, &c., are markedly different from those employed on the Amazon. The trees are tapped mostly on the quarter-section system, which consists of a series of oblique cuts running into a central channel. The latex is collected in a cup connected with the central channel at the base of the tree. Tappings take place daily or on alternate days over certain periods, the tapping consisting in a paring away of a strip of bark of about $\frac{1}{20}$th to $\frac{1}{30}$th of an inch wide along each oblique incision. This is repeated until a certain area of bark has been removed. The portion of the tree so operated on is then allowed a period of rest sufficient for bark renewal, for which 3 to 4 years appears to be an appropriate period. Plantation latex is generally coagulated by the addition of a small quantity of acetic acid. After the coagulum is formed it is removed from the serum and passed through washing rolls, which squeeze out much of the remanent mother liquor and wash out the excess of non-rubber latex constituents. These rolls are of much the same construction as those used in the factory for *washing* (*see* below). The rubber is subsequently hung up to dry in the form of a sheet or crepe, and is frequently 'smoked' during the drying period, coconut husks and hard wood being employed for this purpose. Plantation rubber is invariably shipped bone-dry and is of a translucent light cream to amber colour for ordinary varieties to a dark amber in the case of the smoked goods. Dryness and cleanliness are the characteristics of plantation rubbers which differentiate them sharply from 'wild' descriptions. The estimated production of plantation rubber was in 1908 about 8000 tons, in 1912, 25,000 tons, in 1917, 180,000 tons, and for 1922 over 300,000 tons.

While plantation rubber is practically dry and clean, other crude rubbers of commerce contain varying quantities of moisture and mechanical impurities, such as sand, stones, bark, &c., and frequently an excessive amount of chemical 'impurities,' such as resin, proteid, decomposing animal and vegetable matter, &c. These rubbers must undergo a thorough process of cleansing before they can be used in the factory, and this process consists substantially in passing the rubber, after it has been cut up and steeped in warm water, through washing rolls, whereby it is subjected to a combined process of washing and disintegration. After 'washing' the rubber is dried, and the loss of weight which results from the washing and drying operations is termed 'washing loss.'

The following table shows the average 'washing loss' of a number of the more important commercial varieties :—

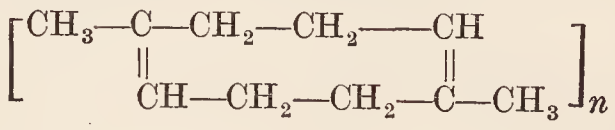
Commercial Name	Washing Loss
Fine Para (hard and soft cure) .	12–20 p.c.
Negro-heads	20–40 ,,
Matto Grosso	15–30 ,,
Maniçoba	28–30 ,,
Mangabeira	30–35 ,,
Congo varieties, better class, such as Upper Congo, Red and Black Kassai, Equateur, &c. . .	6–12 ,,
African niggers (Soudan, Conakry Niger) and Gold Coast 'Lumps,'&c.	15–40 ,,
Assam	15–40 ,,

The use of 'wild' sorts, other than of the 'fine' ' Brazilian grades, has much declined as a result of the development of the plantation industry.

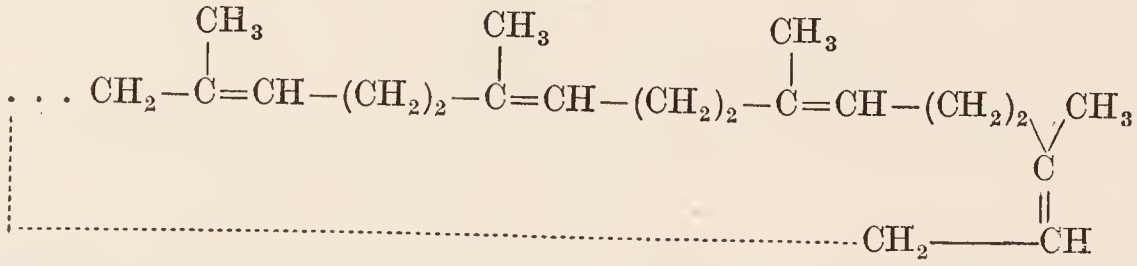
Nature of crude rubber.—Washed commercial *crude* or *raw* rubber consists of 'caoutchouc' or rubber proper *plus* varying quantities of 'impurities,' of which the more important are the *resins* (substances soluble in acetone or alcohol, and, so far as they have been investigated, containing oxygen in varying proportions); *nitrogen* (partly as proteid), *mineral constituents* (principally lime, potash, and magnesium compounds), and *insoluble matter*. The latter in the case of *fine Para* (Spence) is of a fibrous character and contains a high proportion of nitrogen, possibly in the shape of a glyco-protein. It was formerly believed that rubber consisted substantially of two isomeric bodies, the 'adhesive' and the 'nervous' principles respectively, and that the insoluble matter was the 'nervous' moiety, but this certainly is not the case. Many well-prepared rubbers dissolve practically completely in ordinary rubber solvents, and, as Weber showed, the average proportion of 'insoluble' matter in dry fine Para is no more than 3–4 p.c. With regard to the quantities of resin, nitrogen, ash, &c., contained in commercial rubbers, there is a wide variation according to the method of collection, coagulation, and subsequent treatment, many of the 'native' or 'wild' rubbers being prepared in a very primitive manner, and arriving in a wet, sticky or dirty condition; but it may be stated that properly prepared plantation rubbers (*Hevea*) need not contain more than 2–3 p.c. of resin, 0·2–0·4 p.c. of nitrogen, very little insoluble matter (1–2 p.c.), and under 1 p.c. of ash. Fine Para grades generally contain slightly more nitrogen and insoluble matter than plantation grades, calculated in both cases to 'dry substance.' *Castilloa* and *Manihot* may be prepared to contain not more than 3–5 p.c. of

resin, and suitable *Ficus*, *Funtumia*, and *Landolphia* species also yield rubbers not showing more than 5–7 p.c. All the rubbers referred to may be prepared to reach the market in a dry, clean condition, and containing roughly not more than 3–5 p.c. jointly of ash, proteid, and other non-rubber and non-resin constituents.

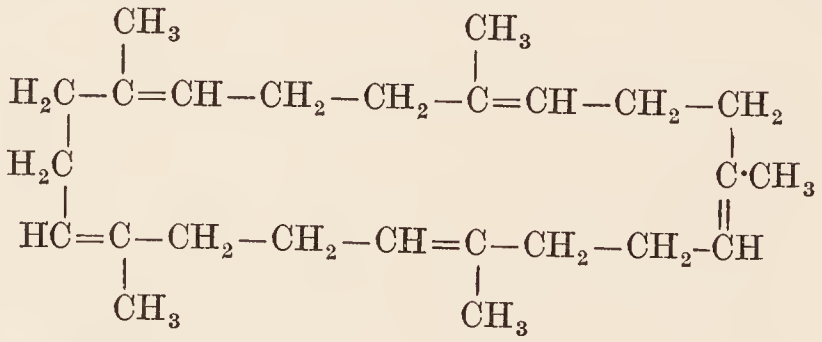
The rubber hydrocarbon.—On highly purifying commercial rubber a material is obtained which approaches very closely to the composition demanded by the formula $(C_5H_8)n$ or $(C_{10}H_{16})n$. The balance of opinion appears to be favourable to the latter. With regard to the constitution of the molecule, Harries, on the basis of work on the fission products of rubber ozonides, regarded it as 1 : 5-dimethyl-cyclo-octadiene



The rubbers obtained from different genera are not, apparently, all identical in structure. Harries found that whereas the ozonides obtainable from purified *Hevea* gave on hydrolysis mainly lævulic aldehyde, with lævulic acid as a secondary product, the reverse was the case with ozonides obtained from gutta-percha and from certain African (*Landolphia* or *Funtumia*) species. The explanation offered is that the ozonide complex occupies a different position relatively to the plane of the eight-ring in space, a *cis*-position in the one, a *trans*-position in the other case. Pickles has suggested that the admitted chemical data regarding the behaviour of the rubber molecule may be best explained by assuming that it does not consist of a number of $C_{10}H_{16}$ rings polymerised to a complex molecule, but of a single ring containing a number of unsaturated C_5H_8 nuclei, *e.g.*:



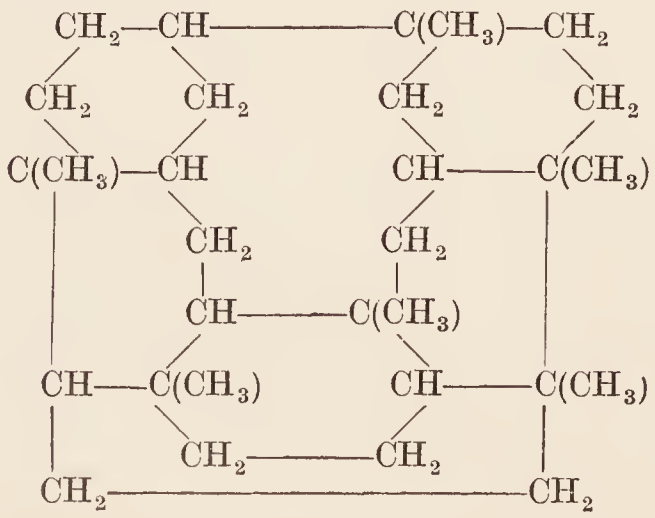
As a result of the later work by Harries (Untersuchungen Ueber die natuerlichen u. Kuenstl. Kautschukarten, Berlin, J. Springer, 1919), he arrived at the conclusion that caoutchouc is a $C_{25}H_{40}$ ring, represented thus:



This formula is mainly based on the observations (*a*) that the molecular weight of the ozonide in benzene agrees reasonably with the formula $C_{25}H_{40}O_{15}$; (*b*) that the thermal dissociation of the hydrochloride is in consonance with it; and (*c*) that among the scission products of the ozonide, diacetyl-propane and triketone appear to occur in a definite ratio.

Cf. Boswell, Hambleton, Parker, and McLaughten (Canadian Chem. and Met. 1922, 6, 237; J. Soc. Chem. Ind. 1923, 63A).

These authors emphasise the difficulty of reconciling a methylcyclo-octadiene structure with the easy production of isoprene, dipentene, and dinitrocumic acid from rubber. They suggest that rubber has a molecule $C_{30}H_{48}$ of the constitution



The freedom from olefinic linkages is held to explain the resistance of caoutchouc to hydrogenation. The above formula is supported by the fact that many reagents convert rubber into compounds containing 25 carbon atoms with elimination of part of the rubber molecule.

According to Kirchhof (Koll. Chem. Beihefte, 1922, 16, 47–87), the analytical data obtained by Harries and his co-workers appear to show that Para caoutchouc has the empirical formula $C_{10}H_{17}$. The African Congo caoutchouc has, like the synthetic isoprene and piperylene caoutchouc, the formula $C_{10}H_{16}$, which has been generally accepted for all forms of caoutchouc. These formulæ are in keeping with the behaviour of these substances during ozonisation and oxozonisation. Because of this formula for Para caoutchouc, it must have a constitution different from that put forward by Harries. The Para caoutchouc hydrocarbon must have an open chain in which the group

$$=CH-CH_2-CH_2-CMe=$$

must appear, but in which other groups must also exist, as shown by the appearance of formic, carbonic, and succinic acids during the decomposition of the ozonide. Here, in part, is the difference between Para caoutchouc and synthetic isoprene caoutchouc (J. Chem. Soc. Absts. 1922, 121, 122, 1945).

If rubber is submitted to dry distillation a

number of isomeric hydrocarbons of the formula C_5H_8 are obtained, among these being *Dipentene* (b.p. 171°) and *Isoprene* (b.p. 37·5°) (*q.v.*). From the latter product a material which appears to be identical with rubber has been synthesised by numerous observers starting with Bouchardat (1875) and Tilden (1882). The polymerising agents which have from time to time been employed by different workers include hydrochloric acid, acetic acid and acetic anhydride, alkalis, metallic sodium and potassium, and various neutral salts. The operation of the polymerising agent has generally been assisted by heat and pressure. Rubber-like substances have also been synthesised from butadiene (and similar hydrocarbons) and from the homologues of this substance and of isoprene by Perkin, Matthews, Ostromisslenski and others.

The manufacture of *commercial synthetic rubber* will only be possible if a suitable low-priced raw material, capable of transformation at a low cost and with a high yield, can be found. So far these conditions do not appear to have been fulfilled.

Properties of crude rubber.—Among the *derivatives* of rubber which are apparently of definite *chemical* composition may be mentioned the ozonide $C_{10}H_{16}(O_3)_2$, oxygen derivatives $C_{10}H_{16}O$ and $C_{10}H_{16}O_3$, the bromides $C_{10}H_{16}Br_4$ and $C_{10}H_{15}Br_5$, the nitrosites $C_{10}H_{16}N_3O_3$, $(C_{10}H_{15}N_3O_8)_2$, $(C_{10}H_{15}N_3O_7)_2$, and $C_{40}H_{62}N_{10}O_{24}$ and the nitrosates $C_{10}H_{12}N_2O_6$ and $C_{10}H_{16}N_2O_4$. For sulphur derivatives *cf.* below under *Vulcanisation.*

Physical properties.—Like most colloids rubber is not (as was generally believed formerly) a structureless mass, but possesses a certain structure varying with the method of preparation and treatment. Freshly coagulated rubber shows reticular structure, the 'net' being composed of the globules originally present in the latex. The globular particles persist even after the rubber has been dried and are visible in rubber solutions made from dried rubber. Films prepared from solutions no longer display reticular structure under ordinary circumstances, but a pronounced network is formed if such films are subjected to the action of diluted sulphur chloride (*cold vulcanised*). The *specific gravity* of clean commercial rubber is about 0·91. On warming the material, the specific gravity gradually decreases and the material becomes soft, then sticky, and finally 'melts.' If crude rubber is cooled it hardens appreciably at temperatures below (about) 50°F., and at (about) 35°–40°F. becomes quite hard and entirely loses its elasticity. Rubber that has been stretched contracts on warming, and heat is absorbed. At ordinary temperatures freshly-cut surfaces of crude rubber adhere to one another. Vulcanised rubber does not appreciably harden or soften on exposure to moderate cold or heat, and is not adhesive. Vulcanisation also improves the mechanical properties of rubber (strength, elasticity, resilience). The physical properties of crude rubber are indeed such that, but for the discovery of the process of vulcanisation, the industry could never have attained to more than very moderate proportions. Like most organic gels crude rubber adsorbs water freely, increasing thereby some 25 p.c. in weight and 15 p.c. in volume. With petroleum and coal-tar hydrocarbons, carbon disulphide, with many chlorine derivatives of methane, ethane, and ethylene, and with essential oils it forms typical colloidal solutions. The most important technical solvents are 'solvent naphtha' (coal tar and shale) and carbon disulphide. Rubber solutions are extremely viscous, but the degree of viscosity depends largely on the nature of the rubber and on its treatment previous to exposure to the solvent. Mechanical working greatly increases the solubility but decreases the viscosity of crude rubber. For manufacturing 'solution' required for spreading, particularly where great strength and covering power are required, the less the material is worked, therefore, the better. Where a solution is required for cementing and sticking objects together, a certain amount of 'working' is desirable, as adhesion is thereby, up to a certain point, increased. There appears to be some connection between the viscosity of a rubber solution and the mechanical properties of the material, and this relationship has been utilised in comparing different samples of rubber of the same species. *Dry* crude rubber is a fairly good non-conductor of electricity and is used to a considerable extent as an inner lapping (next to the wires) in conjunction with an outer lapping of vulcanised rubber, in electric light and power cables and 'flexibles.'

Vulcanisation.—The application of heat to a mixture of rubber and sulphur effects a profound change in the character of the raw material (*see* above). The process of vulcanisation, as this process is termed, is not accompanied by the evolution of any appreciable quantity of sulphuretted hydrogen, and the reaction, therefore, must be either physical (*i.e. adsorption*), or, if chemical, of a purely additive character. Recent research by Spence, which to some extent is confirmed by the work of the author, supports the view that the process, so far as the conversion of 'free' into 'combined' sulphur is concerned, is mainly a chemical one, and only in a very minor degree of an adsorptive character. According to Weber the effects of vulcanisation are not distinctive until the vulcanised material contains 2–2·5 p.c. of combined sulphur (*i.e.* sulphur not removable by solvents or other physical means); this would correspond roughly to $(C_{10}H_{16})_{10}S_2$, and specimens of ebonite (the product obtained if vulcanisation is carried to the ultimate practical limit by means of large quantities of sulphur, prolonged time and high temperatures) prepared with 50, 75, and 100 p.c. of sulphur respectively all yielded products containing approximately 32 p.c. of combined sulphur, corresponding roughly to $C_{10}H_{16}S_2$. Weber concluded that there is a series of products between these extremes, but later work casts serious doubts on the accuracy of these deductions. It is, however, the fact that the amount of combined sulphur stands in some direct relationship, if not ratio, to the amount of sulphur employed and to the time and temperature of the operation. With increasing sulphur, time and temperature, the material after a certain period becomes gradually harder (*i.e.* increases in tensile strength) and decreases in elasticity. Broadly speaking, normal soft rubbers contain 2½–3 p.c. of combined sulphur, hard rubber or ebonite 20–30 p.c. It has, however, been found, that the percentage of

'combined' sulphur in correctly vulcanised rubber is largely dependent on the curing conditions. While, as stated, soft rubbers vulcanised by means of sulphur and heat only, contain 2½–3 p.c. of 'combined,' vulcanisates obtained in the presence of organic 'accelerators' (such as hexamethylene-tetramine, dithio carbamates or formates of various bases, aldehyde ammonia and the like) or catalysts—by means of which curing time may be reduced from hours to minutes—may, although perfectly vulcanised, contain as little as 0·5–1 p.c. of sulphur in the combined state. Such 'accelerators,' it may be added, profoundly influence (improve, in most respects) the quality of the vulcanised goods. An effect similar to that produced by the combined action of sulphur and heat on rubber (*i.e.* the *hot cure*) is obtained by allowing a diluted (3–5 p.c.) of S_2Cl_2 in CS_2 to act on the material. This process, which, owing to the extremely active nature of the reagent employed, can only be employed for vulcanising very thin goods—for if applied to massive articles the exterior would be much over-cured by the time the solution had penetrated to and adequately vulcanised the interior—is called *cold curing* or cold vulcanising, and is accompanied by the binding of sulphur and chlorine, apparently in the same relative proportions as these elements exist in S_2Cl_2. The end product of the reaction is not improbably $(C_{10}H_{16})\begin{matrix}—S—S—\\ \diagdown Cl\ \ Cl\diagup\end{matrix}(C_{10}H_{16})$. Hinrichsen advances the theory that ordinary 'cold-cured' goods consist of solid or semi-solid solutions of this 'end product' in rubber, *plus* varying quantities of adsorbed 'free' sulphur.

The rubber industry proper is of recent origin, the first known reference to the raw material in European literature dates back to 1525, in which year P. Martyr d'Anghiera published a description of some rubber playing balls seen by him in Mexico. It is clear from the records, principally of Spanish and Portuguese writers, that the natives of rubber-bearing districts have for many centuries past recognised the valuable properties of raw rubber, and have made therefrom articles such as playing balls, pouches, boots, and 'waterproof' garments. About 1770 Priestley (the discoverer of oxygen) recommended the use of the material (which at that time was obviously imported from the West Indies) for erasing pencil marks, hence the name 'India-rubber,' and in 1763 Herissant and Macquer sent a memoir dealing with the behaviour of the material towards various solvents to the Paris Academy of Sciences. The latter appears to be the earliest scientific paper on rubber on record. Serious attempts to make use of rubber industrially do not appear to have been made until the beginning of the 19th century. A process, patented by Samuel Peal in 1791 for waterproofing cloth by spreading it (by hand) did not meet with much success, but about 1825, Charles Macintosh of Manchester, having discovered that rubber is soluble in coal tar naphtha, produced 'proofed' garments by a practicable process, and this may be regarded as the starting-point of the modern rubber industry. Nevertheless, it was not until after the process of vulcanisation was discovered by Charles Goodyear of Newhaven, U.S.A., in 1839, and independently by Thomas Hancock of London in 1844, that it showed signs of becoming of first-rate importance. Goodyear mixed masticated crude rubber with finely divided sulphur, and on heating the mass observed the characteristic modification of the properties of the raw material mentioned above. Hancock (who was unaware of Goodyear's work) observed that similar results were obtained by dipping crude rubber into melted sulphur. In 1846 Parkes discovered the process of cold vulcanisation. Among the earlier inventions may be mentioned that of a masticating machine and process by Hancock, which made the manufacture of rubber sheet a practicable operation and much facilitated the production of 'solution.'

Manufacture of rubber goods.—Raw rubber, if we except the best plantation grades, always contains more or less foreign matter (sand, dirt, bark, moisture, soluble proteids, &c.) which must be eliminated before it can be used for manufacturing purposes. The process of removing the impurities referred to is termed '*washing.*' The rubber having been cut into lumps or slabs is first steeped for some hours in warm water to render it pliable and to remove some of the soluble impurities, and is then passed through the washing rollers (Fig. 1). The rolls are corrugated, diamond cut or fluted. and run at a differential speed varying from 6 : 4 to one tooth difference. While many washing machines are still belt-driven, modern practice favours direct electric drive wherever this is possible. Fig. 1 shows a modern machine of this type by David Bridge & Co. A stream of water is kept running upon the rubber during the whole of the operation. The pieces of rubber passing through the rollers are converted by the combined squeezing and disintegrating action of the latter into a rough corrugated sheet. This sheet, which is of a crepe-like texture, is repeatedly passed through the rolls until it is considered to be sufficiently clean and thin. It is then taken to the drying-room, where it is hung on racks until the moisture content has been reduced to approximately 0·25–0·5 p.c. Very low grade, resinous rubbers cannot be dried on racks, but are laid on canvas-covered frames, beneath and through which the air can circulate. Drying rooms are generally heated by means of steam pipes, but the best system is that of passing a current of warm air in a systematic manner through a series of drying chambers. The cooler (relatively) and drier the air the better, for the lower the temperature the less the rubber is inclined to become soft or 'tacky.' At a temperature of about 80°F. most factory-washed rubber can be dried in about 3–4 days if the conditions of ventilation are suitable. When dry the rubber is ready for *mastication* (if to be used for cut sheet, certain grades of thread or 'solution') or for *mixing*, if it is to be manufactured into other classes of goods. As the latter constitute by far the most important branch of rubber manufacture they will be considered first.

Mixing is the term applied to the operation by which sulphur and other materials are incorporated with the rubber. Very few articles are made from rubber and sulphur only, firstly, because of the prohibitive price; and secondly, because 'pure' rubber mixings, on account of their softness and great elasticity, &c., are

unsuitable for the majority of commercial goods. The materials, other than rubber and sulphur, employed in commercial mixings may be broadly classified—there is necessarily much overlapping—as follows :—

(1) '*Fillers*' *or* '*cheapeners*' *pure and simple*, comprising such substances as powdered chalk, barytes, ground rubber waste, 'oil substitute,' 'reclaimed' rubber, &c.

(2) *Materials used for specific purposes.*—(a) *For increasing mechanical strength, i.e.* for hardening or toughening goods, zinc oxide, magnesia (oxide and carbonate), lime, litharge, ground glass, balata, &c.

(b) *For obtaining dense, non-porous mixings* (*i.e.* resistance to water, improvement of dielectric properties), asphalt, bitumen, pitch, ozokerite, &c.

(c) *For improving vulcanising conditions*, litharge, magnesia, lime, antimony sulphide, and organic 'accelerators' (*cf.* below under *Vulcanisation*).

(3) *Pigments*, such as zinc oxide, lithopone, zinc sulphide, antimony sulphide ('golden' and 'crimson sulphide'), mercuric sulphide (*vermilion, cinnabar*), cadmium yellow, chrome yellow, chrome green, prussian blue, &c., and various metallic powders used as 'lustres' or 'bronzes.'

'*Oil substitutes*,' obtained by the action of either S_2Cl_2 in the cold (white substitute) or of sulphur and heat (brown substitute) on colza, rape, maize, and other vegetable oils, are generally employed with a view to reducing the specific gravity of low grade goods.

Reclaimed rubber (*cf.* below under *Waste rubber*) is very useful in the production of moderate priced mixings, particularly in those cases in which large quantities of 'minerals' cannot be employed.

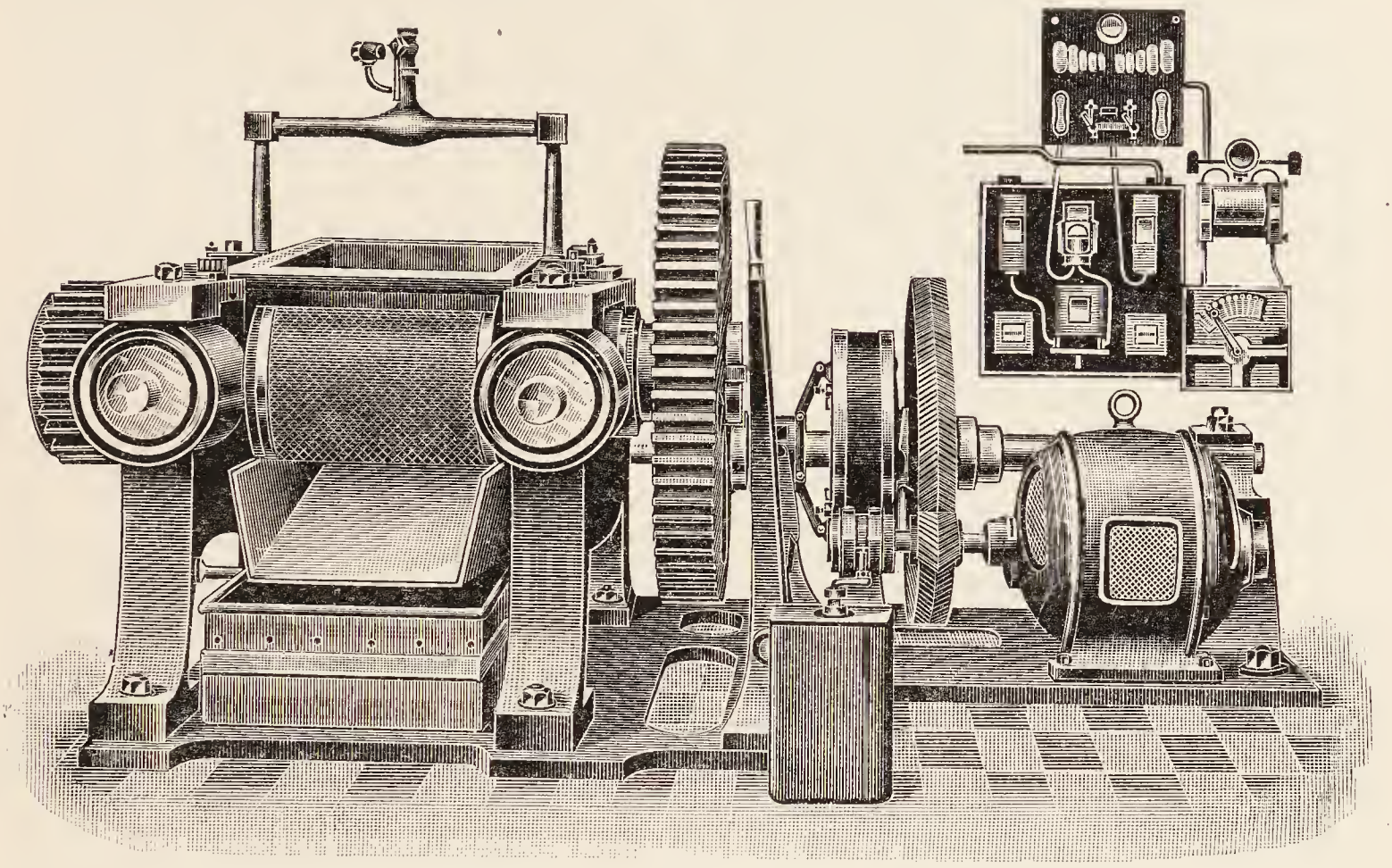


FIG. 1.

Fig. 2 shows a mixing machine, which, in general construction, is similar to the 'washer.' The smooth rolls, which run at different speeds, are hollow and fitted with the necessary connections for heating by steam or cooling with water. Any material falling through the rolls during mixing is caught in a metal tray sustained by appropriate stays. For the purpose of facilitating the removal of sticky mixings from the rolls a 'doctor' (actuated, *cf.* illustration, by gear B) is fitted to the rear roll. The first operation in mixing is that of 'breaking down,' *i.e.* of plasticising the rubber, which is achieved by passing the material repeatedly through the hot rolls, and gradually tightening up the latter. When the rubber is in a thoroughly plastic condition the other materials (reclaimed rubber, ground waste, 'substitute,' other organic fillers, and finally minerals and sulphur) of the mixing are gradually added. The aim of the mixer should be to obtain a thoroughly homogeneous dough without overworking or 'tiring' the rubber. In the case of the manufacture of the vast majority of 'mechanicals,' the dough or compound, while still warm from the mixing operations, is passed through a calender with a view to obtaining the material in homogeneous sheet form of a given thickness. Most calenders consist of a set of three superimposed, steam-heated, very heavy rolls, generally fitted with a change gear so that they may operate either at even or friction speeds (the latter for coating fabrics, the former for producing ordinary sheet). Fig. 3 demonstrates in diagrammatic form the operations of a three-bowl calender. The rubber dough, R, passes between the bowls A and B, and thence between B and C, as indicated. The homogeneous sheet so formed is carried forward by a coarse cloth unwound from roller E. The calendered sheet together with the canvas is rolled upon roller D. The object of using the cloth is to prevent the various layers of rubber from sticking to one another. Calendered sheet or rough 'compound' should be

allowed a period of rest before it is vulcanised, so that it may recover from the somewhat strenuous mixing operation.

Vulcanisation. A. *Hot process.*—According to the class of goods to be made, the 'curing' takes place either in live steam (*open* or *steam*

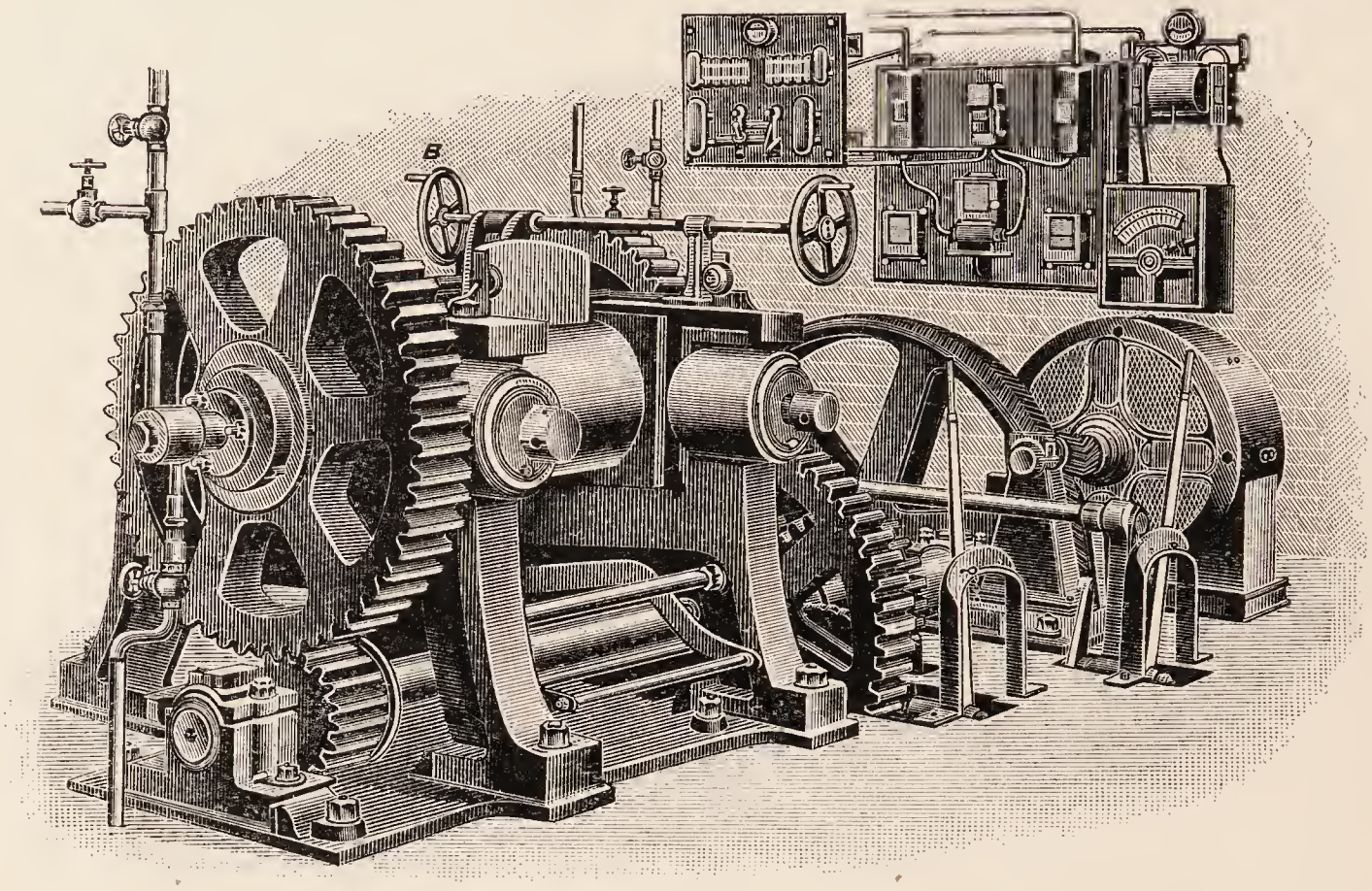


Fig. 2.

cure), in the vulcanising (generally *hydraulic*) press or in hot air (*dry heat cure*). In the *live steam cure* the articles are either cured in moulds (*e.g.* valves, buffers, tyre covers, &c.), or tightly wrapped with canvas (*e.g.* hose of various kinds) or simply imbedded in a thick layer of French

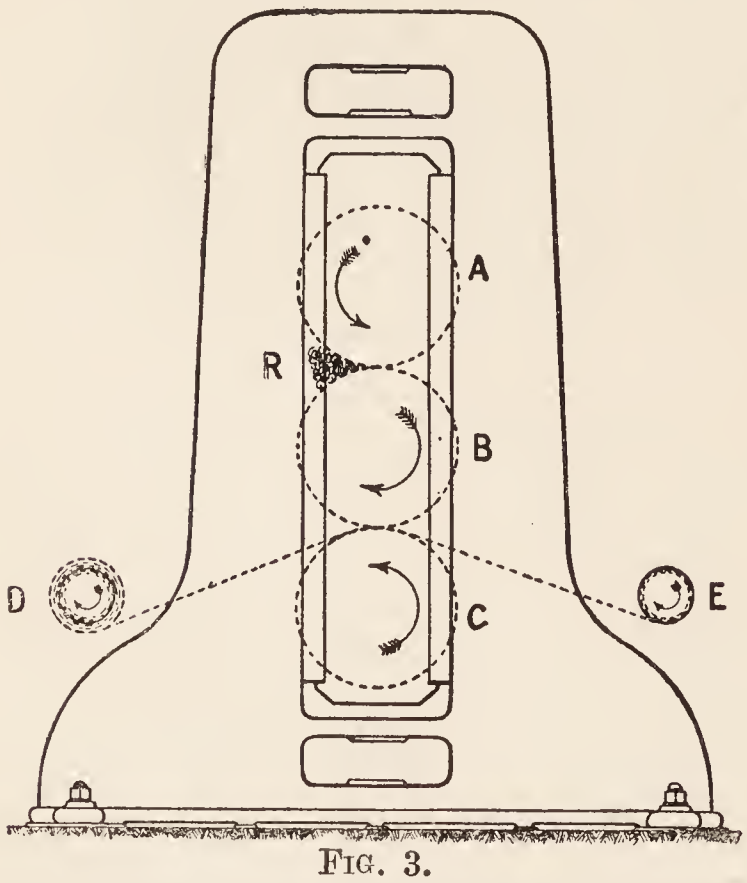


Fig. 3.

chalk. Fig. 4 is a representation of a live steam vulcaniser. These vessels are made of very large size, up to 80 ft. in length and 6 ft. in breadth. In modern practice it is very usual to have a steam jacket fitted to the live cure vessel, a very material equalisation of temperature being brought about in this way. For all practical purposes, then, the live cure vessel is a large autoclave, working with steam and with the usual fittings for control of temperature and pressure, &c. The ordinary vulcanising heats lie between 130° and 160°C.

Press curing.—Fig. 5 is an illustration of a modern hydraulic vulcanising press by Messrs. D. Bridge & Co. The goods, either in moulds, or in the case of sheet built up in a frame, are placed between the hollow steam-heated plates of the press, and pressure is then applied. There is no doubt that the greater the pressure during curing, the better the results, and in this respect the press has a great advantage over the live cure. Other advantages of the press are that relatively large articles of a homogeneous character (*e.g.* sheet) may be economically turned out, and that the pressure can be regulated independently of the temperature. On the other hand, *cæteris paribus*, goods cured more rapidly in live steam than in the press, and it is a somewhat difficult task to maintain the different plates of the press at the same temperature, some unevenness between the lower and upper surfaces of the goods frequently resulting. It is possible to combine the advantages of the live steam cure with those of the press cure by means of the *autoclave press* (*pan-press*). This, in principle, consists of an hydraulic press, the working parts of which are enclosed in an air-tight jacket or chamber to which steam is admitted. For certain classes of goods, *e.g.* tyre covers, the pan press is used to a very considerable extent in modern practice.

Hot-air (dry heat) cure.—This, also known as the Waddington process, is frequently employed, *inter alia*, for curing proofed textiles which were formerly 'cold cured.' The cloth, on to which an appropriate dough of rubber, sulphur, &c. has been frictioned or spread (*see* below), passes over a series of rollers contained in a closed chamber heated by means of a steam jacket or coils. The time and heat are regulated so that

the material may be perfectly cured during the passage through the 'stove.' The dry heat cure is particularly useful for vulcanising goods the appearance or properties of which (*e.g.* goloshes or shoes) would be damaged by steam.

B. *Cold process.*—'Cold curing' consists, substantially, in exposing a thin layer of rubber (either as such, *e.g.* in the case of 'cut sheet,' or frictioned or spread on a fabric) to the action

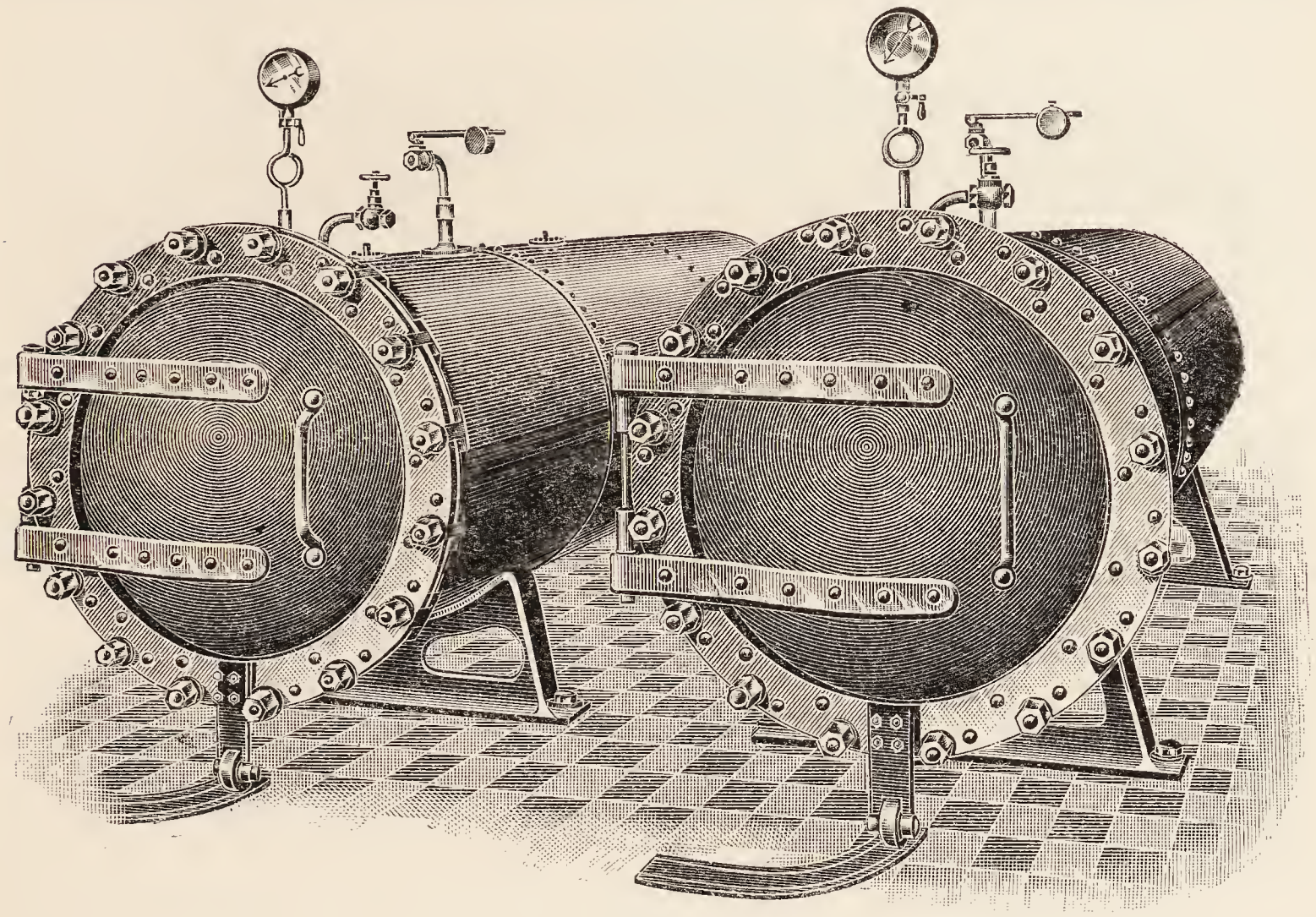


Fig. 4.

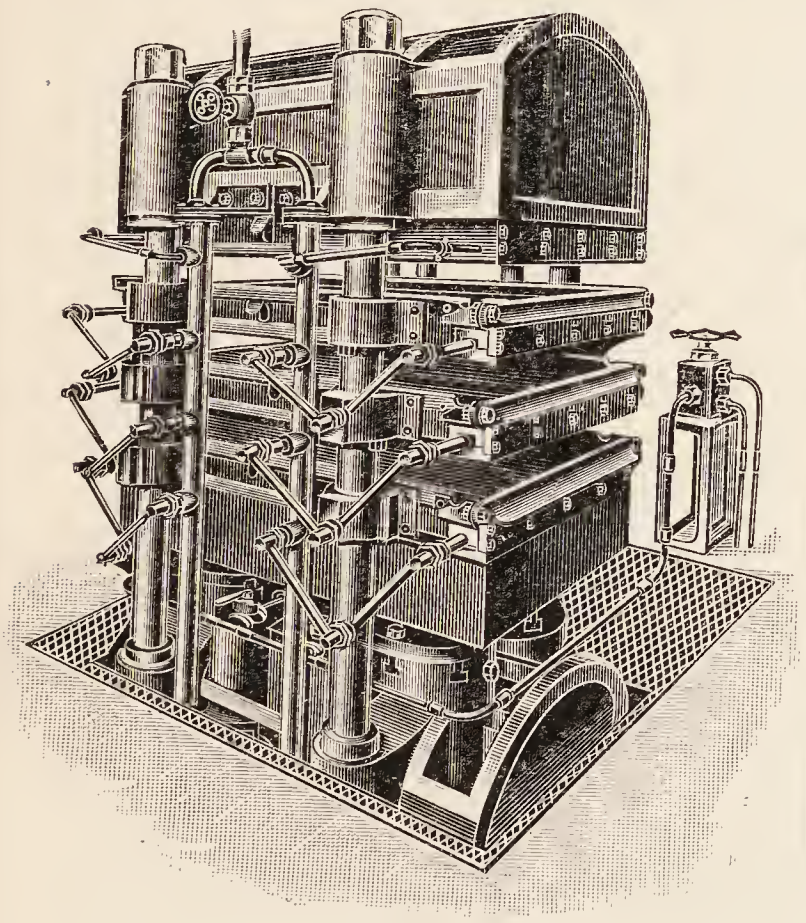


Fig. 5.

of a 2 to 3 p.c. solutions of S_2Cl_2 in CS_2. With the exception of the types of goods cured by 'dry-heat,' practically all proofed garments and fabrics are cold cured. The first operation of cold curing consists in the manufacture of the dough. For this purpose a mixing consisting of rubber only, or of rubber with minerals, pigments, &c., *but without sulphur*, is made in the ordinary way on the mixing rolls, and after rolling out to a thin sheet, is exposed to the action of solvent naphtha in a zinc-lined vessel. In some cases the dough and solvent are worked together by means of rollers. According to the type of 'dough' required more or less of the solvent is employed. After the immersed sheet has absorbed sufficient solvent, it is passed through the 'dough rollers' which run at equal speed and have as their object the production of a mass thoroughly homogeneous in composition. When the solvent and mixing have been thoroughly incorporated the dough is ready for the next operation, viz. that of 'spreading' (*cf.* Fig. 6). The fabric to be coated is placed on roller A, attached to a piece of calico or other cloth, and the latter carried over the roller D, under the knife or 'doctor' G, over table K, and then wrapped round roller H. The dough is placed in the shape of a thick roll or mass upon the fabric between the guides and resting upon the roller D, and against the 'doctor' G. The height, or rather pressure, of the latter (regulated by means of F, F′) above the cloth determines the thickness of the layer of dough spread on the cloth as it passes beneath G. After the cloth has had a layer of dough spread upon it in the manner indicated it passes along the steam-heated chest or table K, the result being that by the time it reaches the 'taking-up' roller H, the solvent has evaporated off. In the majority of cases a number of coats of

'dough' are applied successively, even very thinly spread textures frequently having 15–20 coats applied. The fabrics employed vary a good deal according to the prevailing fashions and are generally specially made for the proofing industry. Fabrics with rubber on one side and

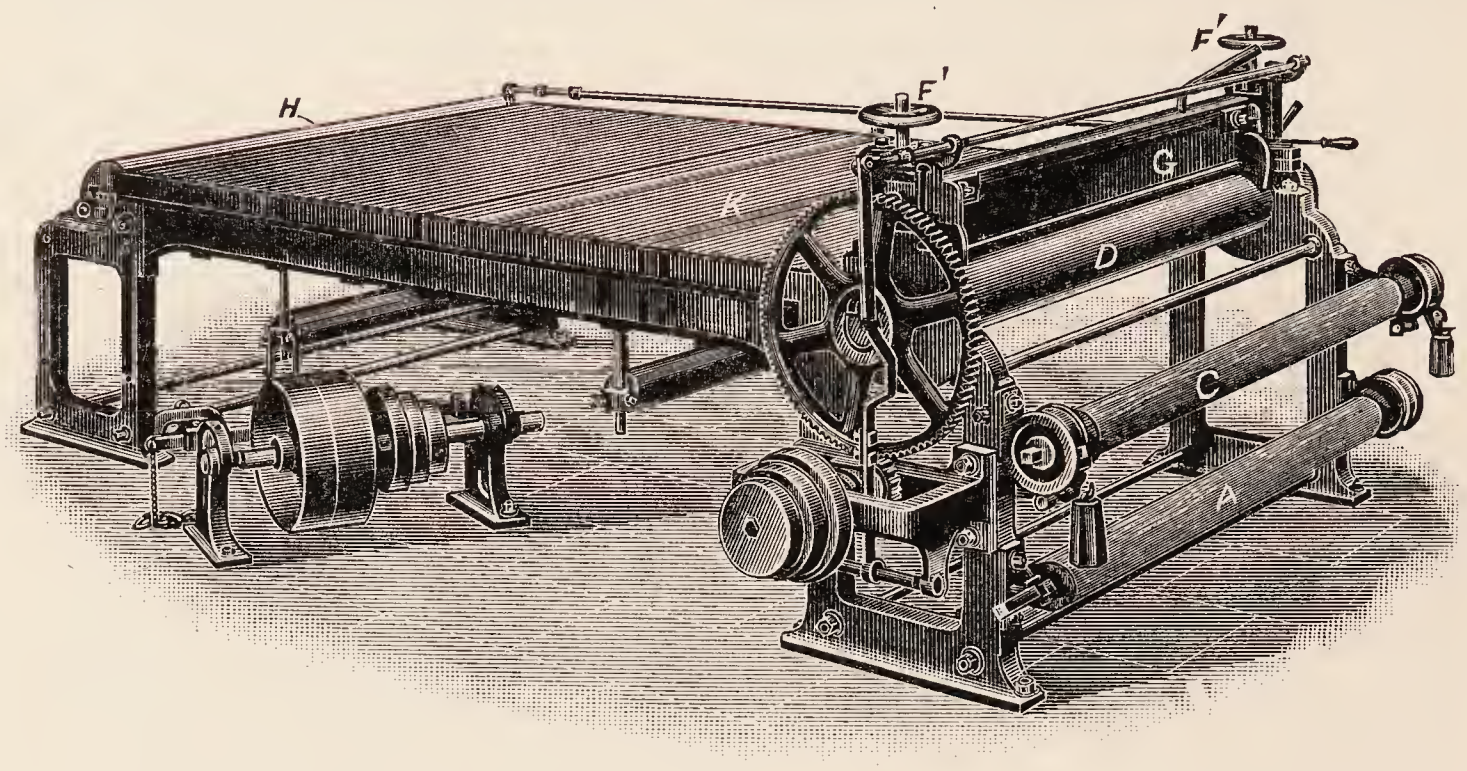


Fig. 6.

cloth on the other are termed 'single texture'; where a layer of rubber is contained between two surfaces of fabric, the term 'double texture' is employed. After 'spreading' has taken place the goods are cured (*i.e.* vulcanised), the

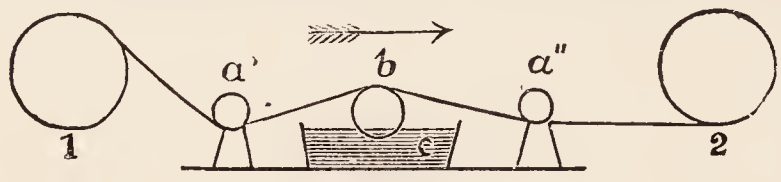


Fig. 7.

sulphur chloride solution being contained in a lead-lined wooden trough. Fig. 7 shows diagrammatically the method of procedure. The goods travel from roller 1 to 2 as indicated, the vulcanising solution in c being applied by means of roller *b*. By the time the goods arrive at roller 2 they are sufficiently cured and dry to roll up. For making 'double textures' the two cloths travel towards one another, and after being cured in separate baths pass through the doubling rollers together before vulcanisation has completely taken place. The method of attaining this result is evident from Fig. 8, in which E and D are the doubling rollers diagrammatically presented. The latter it may be added are also used for uniting fabrics spread with doughs containing sulphur, which are subsequently cured in steam or by dry heat and also for doubling calendered sheet.

Manufacture of Various Classes of Goods.

Cut sheet, which is employed for tobacco-pouches, surgical goods, and similar articles is, or should be, made from the highest grade of

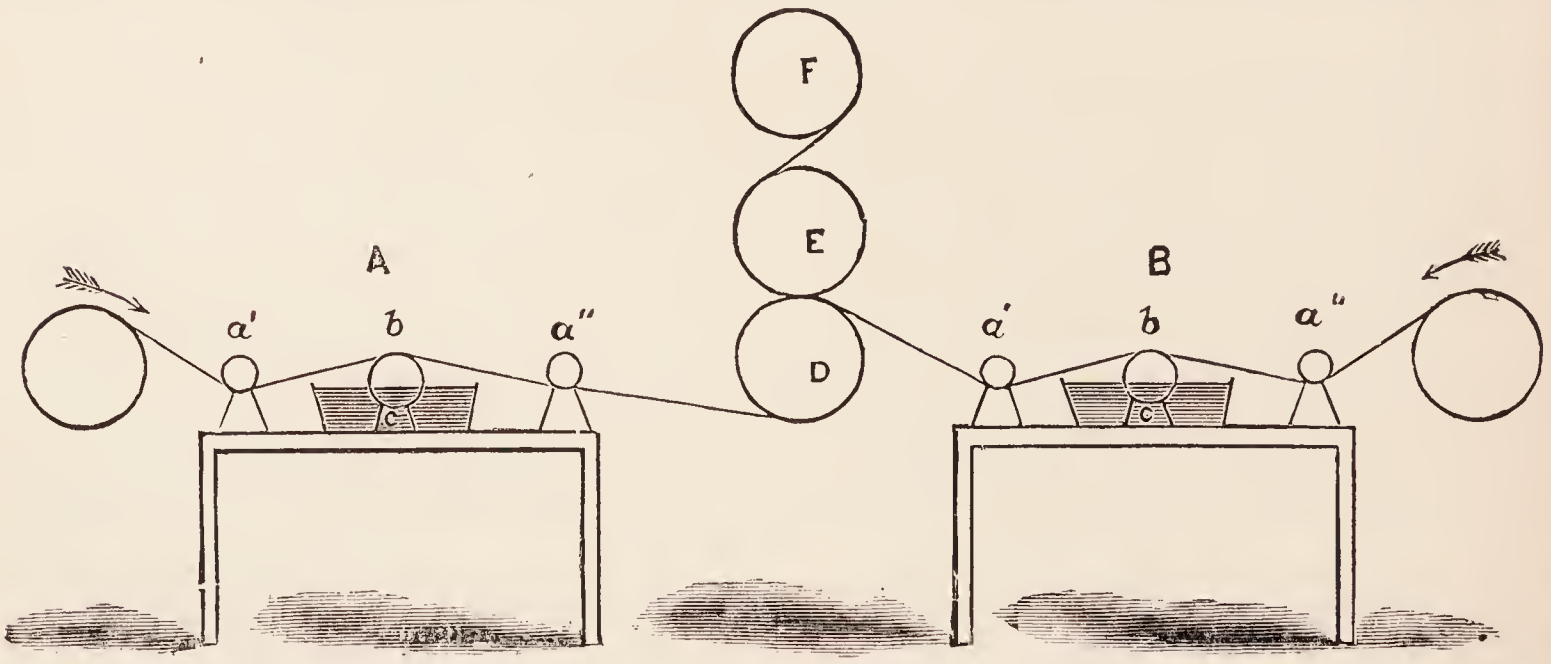


Fig. 8.

materials only. The washed rubber is first masticated in a machine such as is shown in Fig. 9, the essential feature of which (Fig. 10) is a fluted roller B, whereby the rubber (C) is converted into a homogeneous, masticated dough. The hot mass is then compressed by hydraulic power into cylindrical or oblong block moulds, and after the solid blocks of rubber

have been removed from the moulds they are frozen until quite hard. As a rule refrigerating chambers are employed for this purpose nowadays. The frozen blocks are now cut either into sheet has been cut off, the block is raised through a height equal to the thickness of the sheet, preparatory to cutting the next section. Cut sheet goods are generally cold cured, but certain articles, for instance, feeding teats, are sometimes vulcanised by immersion in a sulphur-bath. The cut-sheet trade, partly owing to the expense of manufacture and partly to the improved quality of 'rolled' sheet obtainable by modern calender work, appears to be a declining one.

Elastic thread is mainly employed in the manufacture of 'webbings' (braces, garters, 'spring-side' boots, surgical appliances, &c.)

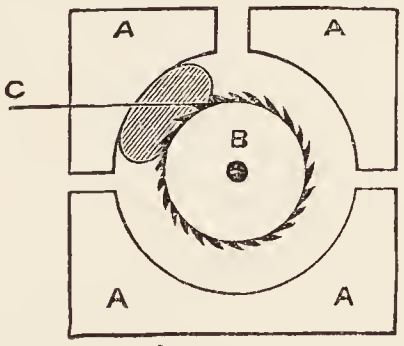


Fig. 10.

and for winding the cores of golf balls. It is made either by spreading or by calendering. In the manufacture of 'spread-thread' a number of coatings of a dough consisting (in the case of the best qualities) substantially of rubber, sulphur, and naphtha are spread or frictioned on to sized calico or on to cloth having a coating of vulcanised rubber as a foundation. The rubber layer is then dusted with French chalk (to prevent adhesion after stripping), stripped from the cloth, made true at the edges, interlined with cloth, and wound upon a drum. The whole is tightly wrapped in cloth and then vulcanised in live steam. When the cure is finished the rubber sheet is removed from the drum, pasted over with a strong solution of shellac in methylated spirit, and while still wet wound upon a roller (which has a foundation of rubber about a quarter of an inch thick to preserve the thread cutting knife from damage) so as to form a cylinder, which dries to a compact block. The rubber is then placed in a cutting lathe and the thread cut to the desired gauge. The final operation consists in removing excess of sulphur and shellac by boiling in a solution of caustic soda. 'Calendered-thread' is made in a manner very similar to 'spread-thread,' the essential difference being that the manufacturer starts with calendered instead of spread sheet.

Tyres. *Solid tyres* (cab tyres, omnibus tyres, rickshaw tyres, &c.) are generally made by 'squirting' an appropriate mixing through a die in the forcing machine, of which Fig. 12 is a diagrammatic representation, or by 'building' up from calendered sheet. In the former method the dough is fed through hopper A into a steam-jacketed chamber in which it is carried forward to the nose-piece C (in which the die is fitted) by means of the screw B. As the tyre emerges from the machine it is coiled on a tray containing French chalk, and is subsequently vulcanised in open steam or hot air. Most heavy solid tyres are cured in moulds, but this method is relatively expensive.

Pneumatic tyres.—Inner tubes are generally made from calendered sheet, although very good results are obtained by some makers by 'squirting.' When calendered sheet is employed it is cut to the desired length and lapped round a mandril, the join being made by means of a slip of rubber and rubber solution. Another method

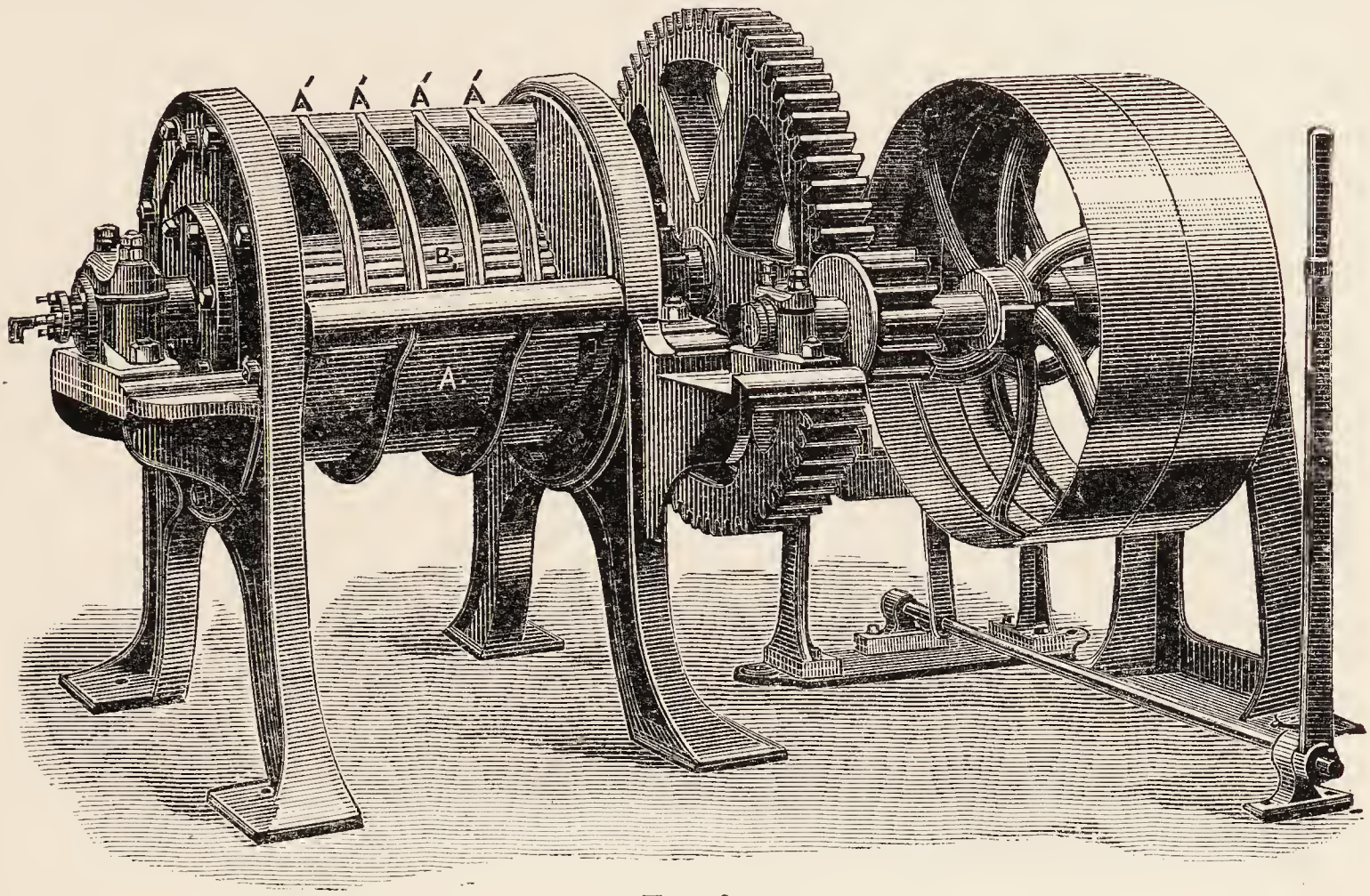


Fig. 9.

consists in building up from two pieces, the joint of the one being opposite to that of the other, or again the calendered sheet may be wound spirally on the mandril and back again, a practically jointless tube resulting. After 'making up' the tube is wrapped tightly on the mandril with cloth and vulcanised in live steam. Subsequently the tube is removed from the mandril and the ends joined up by means of 'solution,' and a cold curing process, or by some equally appropriate method. Occasionally tubes are cured in moulds, the collapse of the tube being prevented by the introduction, prior to curing, of an adequate amount of ammonia or ammonium-carbonate between the walls. This principle is also employed in the manufacture of playing balls and other hollow articles. Pneu-

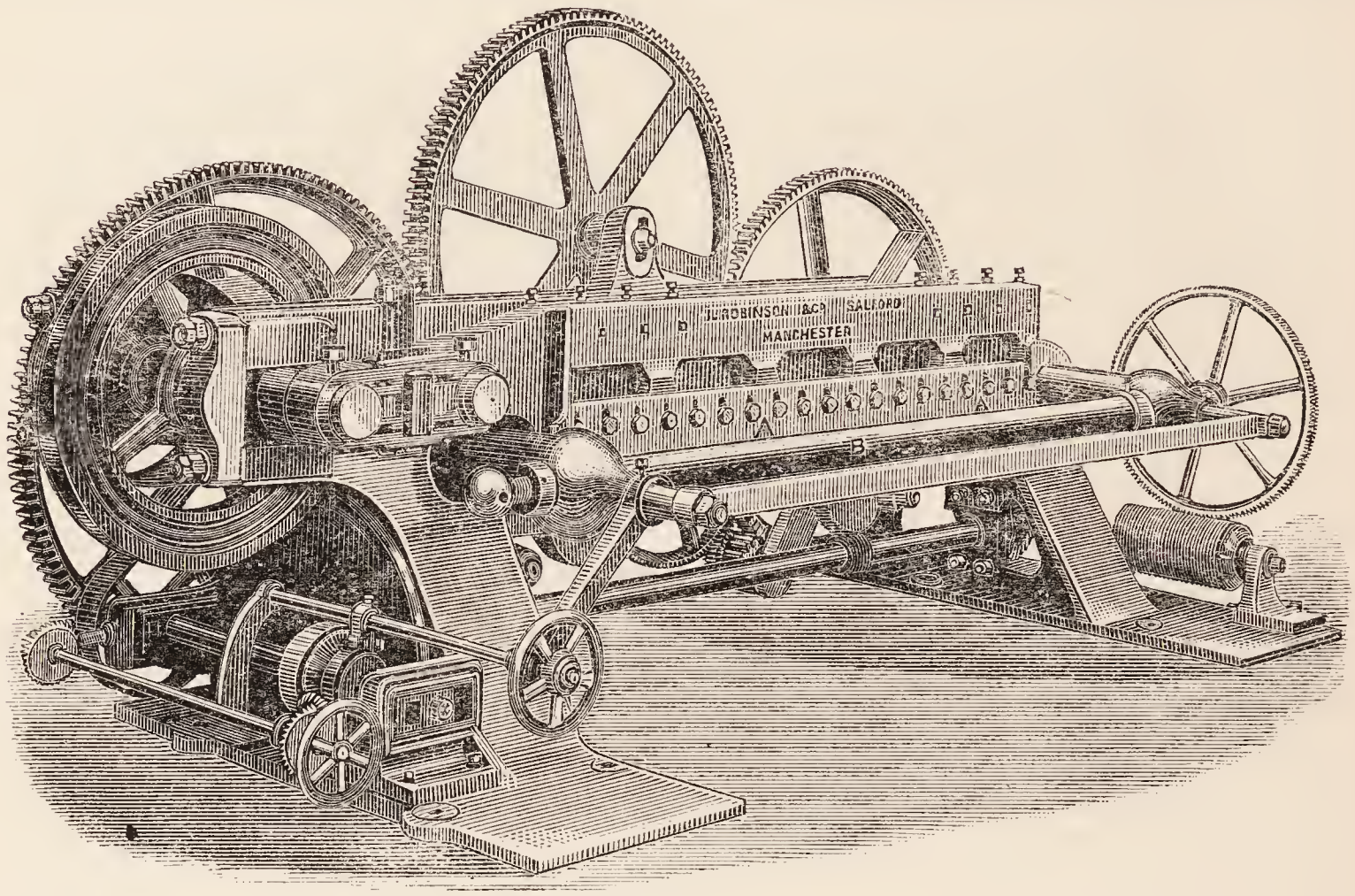


Fig. 11.

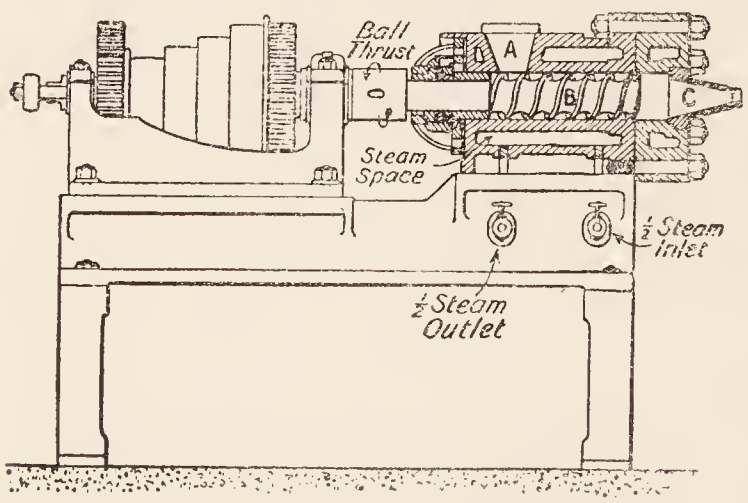


Fig. 12.

matic tyre *covers* are built up on the mandril, mostly by hand (but machines for this purpose have been introduced with some success recently), from layers of proofed canvas and calendered sheet. Vulcanisation of covers is generally carried out in moulds, but occasionally they are mechanically 'wrapped' and then cured in open steam.

Hose of better grades such as pressure hose (*e.g. for liquids*: fire-brigade hose, for pumping, for brewers' use, &c.; for *steam*: railway couplings and breaks, &c.) and vacuum hose (*e.g.* for vacuum brakes, for mining work, &c.) are generally built up from calendered sheet, proofed canvas, and other fabrics, with and without metallic strengthening insertions such as wire, metal bands, &c. Most varieties are made in considerable lengths—the usual 'standard' size is 60 ft.—but special kinds, such as railway vacuum hose, are made up in short eng ths, generally by hand. A number of mechanical appliances are used in making up various grades. Thus ordinary 'friction' hose may be made (*a*) by lapping alternate layers of calendered sheet and canvas round a long mandril horizontally disposed in a hose-making or wrapping machine; (*b*) by drawing a seamless inner tube over the mandril and then lapping or wrapping on canvas; (*c*) by drawing a seamless ('squirted') tube simultaneously with a canvas strip through a machine which folds the latter over the tube; (*d*) by spinning a yarn on to lapped sheet or seamless tube.

Buffers, valves, &c.—Simple buffers ('buffer-springs') are made by vulcanising in moulds calendered sheet which has been lapped round a mandril until the requisite thickness is obtained. In some cases the goods are separately fashioned prior to curing, in others the finished article is obtained by cutting a section of the required thickness from the vulcanised cylinder.

Belting.—A suitable dough is spread or frictioned on to both sides of strong proofed canvas, and after the latter has been cut into strips, a number of the latter are built up until the requisite thickness is obtained. Such belts are vulcanised in long hydraulic presses.

Heels and *heel pads* and many other small articles are stamped from calendered sheet and subsequently vulcanised in moulds.

Rings are either made by 'solutioning' together tape or cord, or by cutting from a tube in the lathe.

Tubing is either 'squirted' or built up by pressing together the bevelled edges of calendered sheet cut to the requisite width.

Ebonite, vulcanite, or hard rubber is the product obtained by vulcanising for a prolonged period (*e.g.* for 6 hours as against 2 hours for soft goods) a mixing containing a high proportion (*e.g.* 25–40 p.c. as against 5–10 p.c. for soft goods) of sulphur. Except when mixed with pigments 'hard rubber' is a material of an ebony-black colour, relatively hard and inelastic and yet—if of good quality—capable of being bent to a considerable degree without breaking. It will take a high polish and may be turned, and, after softening by heat, moulded and pressed. The better grades (*i.e.* those made from rubber, sulphur, and high-class ebonite dust only) are very indifferent towards chemical reagents such as acids and alkalis, and on this account they are largely employed in chemical factories (pumps, pipes, acid cocks, acid-resisting coverings, &c.), for accumulator cases, &c. The ebonite 'mixing' is prepared in substantially the same way as that used for soft rubber goods, but great care must be taken to use materials absolutely free from sand, grit, and similar impurities, and the mixing must be of a very thorough nature. Sheet ebonite is generally, with a view to obtaining a good surface, covered with tinfoil prior to curing, the latter operation taking place in the water-bath between cast-iron plates. Moulded ebonite goods of high grade are cured either in glass or in metal covered with some material possessing an absolutely smooth surface.

Waste rubber.—Many thousands of tons of waste rubber are collected annually, the better grades (*e.g.* motor inner tubes and good 'cold-cured' scrap) fetching relatively high prices. The bulk of it is employed (*a*) after washing and grinding, as a filler in medium to low grade mixings, (*b*) as a basis for the manufacture of 'reclaimed' rubber, (*c*) for the purpose of making 'reformed' articles. The various processes used in the manufacture of *reclaimed* rubber consist substantially of a series of preliminary operations designed to remove all dirt, fibre, metal particles, &c., from the material, followed by treatment under varying conditions with chemical agents such as alkalis, acids, sulphites, &c., with a view to removal of as much as possible of the free sulphur and other non-rubber constituents. While it has been recently stated that 'reclaimed,' from which substantially the whole of the combined—as well as the free—sulphur has been removed, is being manufactured, the writer has not yet come across an article of this nature.

Properties of Vulcanised Rubber.

It will be obvious that vulcanised rubbers must vary enormously *inter se* in their properties, according to the nature of the mixings employed, the methods of 'curing,' &c. Practically all grades, however, are gradually affected by the action of air and light, becoming hard, and finally brittle, but the effect is particularly rapid (*a*) in improperly cured goods, particularly if there is an excess of free sulphur; (*b*) in goods containing a large quantity of mineral fillers and 'reclaimed' or waste rubber. This hardening may be due either to (*a*) 'after-vulcanisation,' or to (*b*) oxidation, or both, but whereas 'after-vulcanisation' is favoured by storage in a warm, dry atmosphere, exposure to light causes, particularly at higher temperatures, rapid oxidation. The oxidation of rubber results in the formation of resinous compounds of which certainly one is soluble in resin solvents, such as acetone or alcohol (Spiller's resin), the other (Burghardt's resin) insoluble. Besides light, air, and (particularly *dry*) heat, rubber is also seriously affected by even slight traces of copper and by some vegetable and mineral oils. The effect of these agents appears to be chiefly that of hastening oxidation, but oils have a solvent action as well. According to Bing the hardening of rubber is always accompanied by the formation of traces of free sulphuric acid. Strong sulphuric and nitric acids rapidly attack even high grade soft rubbers, but towards dilute acids they are relatively stable; but, naturally, mixings containing soluble substances such as zinc oxide, magnesia, calcium carbonate, &c., will be affected according to the quantity of these and the nature, strength, and temperature of the acid in question. High-grade mixings are very stable towards alkalis, but in this case also the presence of substances soluble in or chemically modifiable by the reagent (*e.g.* zinc oxide, antimony sulphide, saponifiable matter, &c.) will cause the goods to be affected.

Physical properties.—Compared with crude rubber, vulcanised rubber is relatively insensitive to changes of temperature. It is relatively impermeable to water and gases, and on this account, as is well known, is largely used in waterproofing, electrical, and balloon industries. Mixings composed of rubber and sulphur only are not the most suitable for resisting water, small quantities of such materials as bitumen, pitch, ozokerite, &c., causing an improvement from this point of view. 'Pure' mixings (V. Henri) are also more susceptible to attack by the actinic rays than articles prepared with suitable mineral fillers, and in the same way crude rubber is more susceptible than the vulcanised article. Rubber is an excellent electrical insulator, and in the soft form is largely used for lighting and power cables and 'flexibles,' and as ebonite for switch-boards, transformer tubes, and so on. High-class cables and flexibles are generally made with a lapping of crude rubber next to the wire, and this is covered with vulcanised strip, the object being to prevent the action of the sulphur in the latter on the conductor. For submarine cables rubber is very little used (excepting for shore end connections running through very shallow water), the main reasons being (*a*) the difficulty of making satisfactory joints, (*b*) the relativcly—as compared with the best gutta-percha—unsatisfactory resistance to water at high pressure, (*c*) the difficulty of entirely preventing any action of the sulphur on the conductor.

Mechanical properties.—Rubber as an industrial material is chiefly valued on account of its mechanical properties. These will, naturally, vary with the nature of the mixing and cure, but within reasonable limits high-grade soft rubbers

conform to certain general laws in a manner indicating the predominant and specific influence of the basis material. Rubber does not obey Hook's law, the modulus of elasticity being a variable, and not as with metals, a constant quantity. Rubber is the only material which, with increasing stress shows an *increasing* resistance to stretching. If a rubber stress-strain curve is drawn with the stresses calculated to the original cross-section of the test-piece, a characteristic inversion of sine at a point corresponding roughly to an extension of the material to twice its original length, takes place. In other words, it would appear that distensibility increases to a maximum and then decreases. But Hatschek has shown that if the stresses are plotted to actual cross-section (corresponding to the elongation) the 'point' of inflection, as it has been called, disappears, and there is a constant and fairly regular increase in resistance to stretching. The analytical construction of the (soft) rubber curve corresponds to the equation $y=\frac{ax}{b+x}$, that of a rectangular hyperbola, passing through the origin and having for asymptotes parallels to the axes with the equations $y=a$ and $x=-b$. Schidrowitz and Goldsbrough have shown that the process of vulcanisation displays the following characteristics: (*a*) it is physically and mechanically of a definitely progressive character, and its progress can be accurately represented by a series of stress-strain curves, which as curing proceeds, come down the paper in regular fashion and do not intersect at any point. The latter part of these curves are (in soft rubber cured with a sufficiency of sulphur) parallel; that is to say, the rate of stretch decreases with increasing loads, *and is independent of the state of cure.* (*b*) The slope (or *type*, as it has been called) of the latter part of the curves varies for different (raw) rubbers, and is regarded as a measure of one of the 'inner' properties of the material—*i.e.* of resistance to stretching or toughness. Rubbers which have been under-cured exhibit a relatively high extensibility and low breaking strain, over-cured rubbers (*cæteris paribus*) the reverse. When both extensibility and breaking strain are low, the presence of a considerable proportion of low-grade rubber or of non-mineral fillers (*i.e.* waste or reclaimed rubber, &c.) is indicated. Where the extensibility and 'combined' sulphur content are high, but the strength poor, the cause may be the over-working of the rubber on the rolls. Soft rubbers of fair to high class should possess a breaking strain of 1500–2500 lbs. per square inch, and an elongation at break (taking the original length as=1) of 8–10. Medium soft to hardish rubbers of the same grades should break at 1200–3000 lbs., and exhibit an elongation of 6–8.

Compression.—Rubber is practically incompressible, the figures obtained by different authorities being substantially of the same order as those for water. The volume of a mass of rubber, therefore, remains constant, whatever deformation it may undergo.

Hysteresis.—If a strip of rubber is stressed to a point short of the break and the load is then removed, it will not return absolutely to its original length, but, according to the nature of the mixing and load applied, will show a certain amount of 'set.' That is to say, the retraction curve will not coincide with the elongation curve, the two forming a loop. This effect has been termed *hysteresis* on account of its analogy to the phenomenon associated with the demagnetisation of iron. The nature and area of these *hysteresis* loops (Schwartz and others) afford valuable data regarding the quality of a rubber. (Chemistry and Mechanics of Vulcanisation, *cf.* Twiss, J. Soc. Chem. Ind. 1917, P. 782; Schidrowitz, Chemical Age, 1921, March 5th to April 2nd; *ibid.* and collaborators, J. Soc. Chem. Ind. 1919, 347; *ibid.* 1921, 268 T.; *ibid.* 1922, 324 T.; Hatschek, *idem.* 1921, 253 T.; Whitby, *l.c. infra.*)

Technical Examination of Rubber Goods.

Crude rubber and vulcanised goods are frequently (on the part of the seller mainly with a view to control and improvement of manufacture, on the part of the buyer from the standpoint of ascertaining value or quality or of controlling contracts) submitted to chemical, physical, and mechanical tests.

Crude rubber.—Substantially, the value of a crude rubber depends (*a*) on the quantity of actual rubber contained; (*b*) on the quality of the latter; (*c*) on the nature of such of the substances other than rubber which are non-removable by the ordinary works methods of purification (steeping and washing). The quantity of rubber is generally estimated by difference, determinations of moisture, resin, ash, nitrogen, and of insoluble matter giving the necessary data. There is a certain amount of overlapping between the 'ash,' 'nitrogen' (generally calculated as proteid), and 'insoluble' matter, which must be taken into consideration. The estimations referred to are, if possible, carried out on *washed* goods, and, naturally, when working in this way, 'washing loss' must be allowed for. With regard to the quality of the rubber, some basis of comparison between different samples of the *same species* is afforded by a determination of the viscosity of their solutions, but the best method undoubtedly is that of vulcanisation. In ordinary vulcanising experiments the aim should be to obtain the *best* cure, and this varies considerably for different rubbers. Vulcanised samples should be tested certainly in regard to rate of cure, their mechanical properties, and, also, where possible, in regard to behaviour on storage. In special cases, of course, chemical and physical tests (*cf.* below) will be useful.

Vulcanised goods.—Chemical analysis and physical and mechanical tests are employed by the manufacturer with a view to matching samples and for controlling, improving, and investigating defects in manufacture. The buyer, as a rule, tests the goods in order to ascertain whether they conform to a sample, contract, or specification.

Chemical analysis is employed with a view to determine *inter alia* (*a*) free and combined sulphur; (*b*) substances soluble in acetone (rubber resins, oils, paraffin, &c.); (*c*) substances such as *bitumen, pitch, and tar*; (*d*) saponifiable matter (*'substitutes' made from vegetable oils, &c.*); (*e*) other 'fillers' (chiefly *mineral matter*, occasionally *fibres, free carbon, starch*); and (*f*)

rubber, the presence of old (scrap) rubber or 'reclaimed.' 'Rubber' is generally determined by difference, the presence of 'reclaimed' or waste rubber may generally be inferred with considerable certainty if the 'combined' sulphur is high, the acetone extract abnormal, and the tensile tests show poor results.

Physical and physico-chemical tests which have practical value include (*a*) the determination of the effects of various reagents such as acids, alkalis, oils, &c., on the weight, volume, and mechanical properties of the material; (*b*) steam and dry heat tests; (*c*) electrical tests such as specific resistivity, surface resistance, and dielectric strength; (*d*) specific gravity, porosity, permeability, bursting tests, &c.

Mechanical tests comprise *inter alia* general tensile tests (*breaking strain, elongation at break, nature of curves at intermediate loads, elongation at constant load* and vice versa, *repeated stretchings, hysteresis tests,* &c.), compression tests (*compressions corresponding to specific loads, repeated compression, hammer test, recovery after compression for specific time,* &c.), abrasion tests, hardness tests, and elasticity tests.

The following is a list of a few of the more important works dealing with subjects referred to in the above article.

Bibliography. (*a*) *General.*—The Reign of Rubber (W. C. Geer, Allen and Unwin, 1923). Rubber (P. Schidrowitz, Methuen, 1911). India-Rubber and its Manufacture (H. L. Terry, Constable, 1907).

(*b*) *Cultural* and *botanical.*—Plantation Rubber and the Testing of Rubber (S. G. Whitby, Longmans, Green & Co., 1921). Estate Rubber (O. de Vries, Ruygrok & Co., 1920). Hevea Braziliensis, or Para Rubber (H. Wright, Maclaren & Co., 1912). The Physiology and Diseases of Hevea Brazilienis (T. Petch, Dulau, 1911).

(*c*) *Manufacture.*—Pneumatic Tyres (H. C. Pearson, India-Rubber Publishing Co., 1922). Rubber Goods Manufacture (Anon., Maclaren, 1920). Rubber Machinery (H. C. Pearson, India-Rubber World, 1915). Crude Rubber and Compounding Ingredients (H. C. Pearson, India-Rubber Publishing Co., 1910). The Manufacture of Rubber Goods (Heil and Esch; Engl. ed., Griffin, 1909).

(*d*) *Chemistry, analysis,* and *testing.*—The Chemistry of Rubber (B. D. W. Luff, E. Benn, 1923). The Analysis of Rubber (Tuttle, The Chemical Catalog. Co. 1922). Whitby (*l.c. supra*). De Vries (*l.c. supra*). India-Rubber Laboratory Practice (W. A. Caspari, Macmillan, 1914). The Chemistry of the Rubber Industry (H. E. Potts, Constable, 1912). The Chemistry of India-Rubber (C. O. Weber, Griffin, 1902).

P. S.

Synthetic Rubber. Elastic colloids more or less similar in character to natural rubber, are formed by the polymerisation of butadiene ($CH_2 : CH{\cdot}CH : CH_2$) and its homologues, especially isoprene (methylbutadiene) and dimethylbutadiene. The polymerisation of these unsaturated hydrocarbons may take place spontaneously, either at the ordinary temperature or on heating, but the process is greatly accelerated by the presence of catalysts, amongst which sodium, glacial acetic acid, and both inorganic and organic peroxides, *e.g.* sodium peroxide and benzoyl peroxide, appear to be very effective. The character of the synthetic rubber depends not only upon the composition of the hydrocarbon from which it is prepared, but also upon the nature of the catalyst employed. Thus Harries has prepared two series of synthetic rubbers by the polymcrisation of butadiene, isoprene, &c., using on the one hand sodium and on the other acetic acid as the catalyst. The products obtained by the use of sodium, although resembling natural rubber in their physical properties, do not behave similarly when subjected to chemical treatment; the acetic acid products present a closer analogy from a chemical standpoint, but are inferior to natural rubber in physical properties. Harries, indeed, holds the view that 'normal' rubber obtained from isoprene with the aid of acetic acid is identical with that occurring in nature, since the ozonide derived from the former behaves on hydrolysis in the same way as the ozonide of natural caoutchouc. Ostromisslenski, on the other hand, claims that the rubber formed by the polymerisation of β-myrcene (a hydrocarbon of the formula $C_{10}H_{12}$ prepared from isoprene) differs from all other synthetic products and is probably identical with natural Para rubber. It still remains doubtful, however, whether any of the synthetic products, even those derived from isoprene, are to be regarded as true caoutchouc.

The demand for rubber brought about by war conditions and the shortage in Germany gave a great impetus to the production of synthetic rubber in that country, and a factory was erected capable of producing 2000 tons annually of 'methyl rubber' from dimethylbutadiene. The product was at first not wholly satisfactory, for, being sensitive to atmospheric oxidation, it deteriorated rapidly, and, moreover, was somewhat refractory towards vulcanisation. These objectionable qualities have, it is said, been in large part removed by improvements in manufacturing processes. By addition of organic bases, especially piperidine and similar compounds, a useful hard rubber (vulcanite) can be produced which is claimed to be equal in firmness and durability to the natural material and even superior for electrical insulating purposes. Soft rubber is more difficult to make, for at ordinary temperatures the product is not elastic but of a tough leathery nature, and even when warmed has not the necessary resilience. The addition of such substances as dimethylaniline considerably improves the elasticity, and a satisfactory soft rubber can now be prepared which is said to be successfully used for tyres for heavy road motors.

Isoprene and the other unsaturated hydrocarbons which serve as the raw material for the production of synthetic rubber can be prepared by many different methods, most of which, however, must be ruled out on the ground of expense. Amongst the materials available for the synthesis of these hydrocarbons, the supply of which is fairly abundant, the following may be mentioned. The pentanes contained in the low boiling fractions of American petroleum can be converted into isoprene by the preparation of their dichloro- derivatives and the subsequent elimination of two molecules of hydrogen chloride from these. The fraction of Russian

petroleum which boils above 300° when cracked under high pressure yields a fair amount of isoprene. Amyl alcohols, produced from starch by fermentation under special conditions, can be converted into dichloropentanes and then into isoprene. When a mixture of ethyl alcohol and acetaldehyde is passed over heated alumina condensation takes place with elimination of water and formation of butadiene. Cellulose is another possible source; sawdust subjected to the hydrolytic action of dilute acids under pressure yields considerable quantities of lævulinic acid, which with the aid of phosphorus trisulphide can be converted into methylthiophen, and when this compound mixed with hydrogen is passed over heated copper, hydrogen sulphide is eliminated and isoprene formed. Acetone prepared from acetylene was used in Germany during the war as a source of synthetic rubber; the acetone was reduced by means of aluminium to pinacone, which was then converted into dimethylbutadiene. Benzene can be successively converted into cyclohexane, chlorocyclohexane, and tetrahydrobenzene, and the last compound when heated breaks down into ethylene and butadiene.

Taking into account possible improvements in the production of natural rubber, it appears more than doubtful whether the synthetic product can compete with it as regards price; it is generally agreed that unless the latter can be put on the market at about 1*s.* 3*d.* per lb. there is little chance of the natural material being superseded. At the present time manufacture appears to have been entirely abandoned.

For more detailed information regarding the production of synthetic rubber the following papers should be consulted: Perkin, J. Soc. Chem. Ind. 1912, 31, 616; Potts, *ibid.* 1913, 32, 564; Luff, *ibid.* 1916, 35, 983; Board of Trade Journal, 1918, 101, 403; Staudinger, Schweiz. Chem.-Zeit. 1919, 1, 1, 28, 60.

G. G. H.

RUBELLITE *v.* TOURMALINE.

RUBIA KHASIANA. According to Watt (Dictionary of the Economic Products of India, vol. vi. 571), there exists a variety of the *R. cordifolia* (Linn.) to which he has assigned the name of *R. khasiana.* This form, according also to Watt, is the richest in madder dye principle. It is occasionally met with in Sikkim, but attains its greatest development eastward in the Khásia and Naga hills. It seems nowhere to be met with to the west of Sikkim. This dyestuff, according to Perkin and Hummel, yields colours precisely similar to those given by *R. cordifolia* and *R. sikkimensis* (Kurz), but it possesses a somewhat greater colouring power than either (J. Soc. Chem. Ind. 1894, 13, 348).

A. G. P.

RUBIA SIKKIMENSIS (Kurz). This Indian dyestuff is closely allied botanically to *Rubia cordifolia* (Linn.); the dried root, which has a rough fluted appearance, is covered with a thick powdery layer of a grey pith-like substance, and looks altogether different from the round, smooth, straight roots of *R. cordifolia.* It occurs along with the allied species above mentioned in Sikkim and eastward to the Khásia and Naga hills, where it is perhaps the most common as it is certainly the largest and most handsome species Although the root has long been collected and sold in the bazaars at Darjeeling, the plant was not named or even known to exist prior to 1874, having escaped the attention of botanists, who appear to have mistaken it for *R. cordifolia.* The Lepchas of Sikkim do not appear to know that *R. sikkimensis* yields the madder dye, but in the Naga hills and in Manipur this species alone supplies the brilliant red dye used by the hill tribes (see Dyes and Tans of India, 154; Special Catalogue of Exhibits by the Government of India, Colonial and Indian Exhibition, 1886).

The examination of this root, by an identical process to that detailed in connection with Munjeet (*R. cordifolia*), has indicated that the phenolic constituents are *purpurin*, *mungistin* and *purpuroxanthin.* A trace of a red colouring matter approximating to $C_{15}H_8O_6$ in formula was also isolated, but the individuality of this compound has not been definitely established.

Dyeing properties.—The application of *R. sikkimensis* root in dyeing presents no difficulty.

Calico printed with iron and alumina mordants may be dyed without any addition of calcium carbonate or acetate to the bath since there is a sufficiency of calcium salt naturally present in the root. Generally speaking, the colours with the different mordants are similar to those obtained from madder, but the reds and chocolates are much bluer being devoid of yellow, and the lilacs are decidedly greyer. The colours, however, are precisely similar to those obtained from *R. cordifolia*, the latter possessing nearly a half more dyeing power.

Comparing the colours on ordinary stripe mordanted calico given by pure purpurin and *R. sikkimensis*, a very marked difference is noticeable; the former gives very yellowish-reds and chocolates, full pinks and purplish lilacs, while the latter yields very bluish-reds and chocolates, bare pinks and greyish lilacs.

The dyeing power of *R. sikkimensis* is equivalent to its containing 0·37–0·5 p.c. purpurin (Perkin and Hummel, Chem. Soc. Trans. 1883, 63, 1157).

A. G. P.

RUBIACIC ACID, RUBIACIN, RUBIADIN. *Rubianin v.* MADDER.

RUBIADIN GLUCOSIDE *v.* GLUCOSIDES.

RUBIADIPIN, RUBIAFIN *v.* MADDER.

RUBIANIC ACID *v.* GLUCOSIDES; ALIZARIN AND ALLIED COLOURING MATTERS.

RUBIDEHYDRAN *v.* MADDER.

RUBIDINE *v.* AZO- COLOURING MATTERS.

RUBIDIUM. Rb. At.wt. 85·45 was discovered by Bunsen and Kirchoff by means of the spectroscope in 1861. In small quantities, rubidium is very widely distributed in nature; it occurs in many minerals such as *leucite*, *triphylite*, *porphyrite*, *mica*, *orthoclase*, *carnallite* (Feit and Kubierschky, Chem. Zeit. 1892, 16, 335); in nearly all iron ores, in some aluminous minerals and in many meteorites (Hartley and Ramage, Chem. Soc. Trans. 1897, 533, 547). It is also present in many mineral springs, in sea water, seaweed, beetroot, tobacco, in various kinds of coffee and tea, in crude cream of tartar, in potashes from various sources and in the ash of the oak and of some beech trees, but rubidium cannot replace potassium as a plant food. For modes of separation from its minerals and from cæsium, *v.* Muthmann (Ber.

1894, 26, 1019, 1425); Formánek (Oesterr. Chem. Zeit. 1899, 2, 309); Feit and Kubierschky (*l.c.*); Lemoine (Bull. Assoc. Belge des Chim. [9] 12, 344); Wells (Amer. Chem. J. 1901, 26, 265); Archibald (Chem. Soc. Trans. 1904, 776). The metal can be obtained by heating a mixture of sugar charcoal, ignited acid rubidium tartrate and calcium carbonate at a white heat, or by distilling the hydroxide with magnesium (Erdmann and Köthner, Annalen, 1896, 294, 55).

Hackspill prepared metallic rubidium by heating the chloride with metallic calcium in an iron boat in a vacuum and then distilling off the metal (Compt. rend. 1905, 141, 106).

Rubidium is a silver white readily volatile metal of sp.gr. 1·5248 (Hackspill, Compt. rend. 1911, 152, 259), m.p. 38·5° and b.p. 696°; coefficient of expansion of the solid metal 0·00027; of the liquid metal, between 40° and 140°, 0·000339; specific heat (solid) 0·0802 +0·000153*t*; (liquid) 0·0921–0·000026t; heat of fusion 6·144; ratio of atomic heat of fusion to abs. m.p. 1·68 (Rengade, Compt. rend. 1913, 156, 1897). Like potassium, it forms amalgams with mercury, an explosive compound with carbon monoxide, oxidises rapidly in air and decomposes in water at −108° with liberation of hydrogen. Many of the minerals in which it occurs and its salts are radioactive (Campbell, Proc. Cambs. Philos. Soc. 1909, 15, 11; Strong, Amer. Chem. J. 1909, 42, 147; Büchner, Proc. K. Akad. Wetensch, Amsterdam, 1909, 12, 154). According to Aston rubidium is a mixture of two isotopes of masses 85 and 87.

The salts of rubidium are isomorphous with, and very similar to, the corresponding potassium, ammonium, and cæsium salts. Rubidium salts are radioactive. Comparative experiments made by Hahn and Rothenbach (Physikal. Zeits. 1919, 26, 194) on the penetration of the rays showed that the rubidium β-rays are slightly more penetrating than those of UX_1, the total activity of these rays compared with that of UX_1 rays being as 1 to 15. Rubidium is at most only ten times weaker than an equal weight of thorium. Potassium is found to be much weaker than rubidium, and no activity could be detected with cæsium salts (*cf.* Büchner, Proc. K. Akad.; Wetensch, Amsterdam, 1912, 15, 22).

The *oxide* Rb_2O (Rengade, Compt. rend. 1906, 143, 1152), also the *oxides*, Rb_2O_2, Rb_2O_4, Rb_2O_3 (Rengade, *ibid.* 1906, 142, 1533; 1907, 144, 920), and the hydroxide Rb(OH), a greyish-white deliquescent mass (Forcrand, Compt. rend. 1906, 142, 1252), have been prepared.

Rubidium peroxide hydrate $RbO{\cdot}OH,H_2O_2$ forms snow-white deliquescent crystals, stable below 0°, but decomposes violently at the ordinary temperature with evolution of oxygen and deposition of a hydrated form of the oxide Rb_2O_4 (Peltner, Ber. 1909, 42, 1777).

Rubidium hydride RbH is formed when the metal is heated in a current of hydrogen at 300°. It forms colourless prismatic needles and is readily attacked by the halogens, oxygen, and sulphur. With phosphorus it yields phosphine; with nitrogen, a mixture of the nitride and amide is formed. When heated with carbon dioxide it yields the formate, and with sulphur dioxide it forms a mixture of sulphide and sulphate at ordinary pressure, and a hyposulphite, $Rb_2S_2O_4$, at diminished pressure. With ammonia, the hydride reacts thus:

$$RbH+NH_3=RbNH_2+H_2$$

(Moissan, Compt. rend. 1903, 136, 587; Ephraim and Michel, Helv. Chim. Acta, 1921, 4, 762).

Rubidium chloride RbCl, forming glittering cubes, and the corresponding bromides and iodides, readily unite with the halides of a large number of metals forming crystalline double salts (Vermande, Pharm. Weekblad. 1918, 55, 1131); similar double salts are also formed by many other rubidium compounds (Biltz and Herms. Ber. 1907, 40, 974; Weinland and Dinkelacker, Zeitsch. anorg. Chem. 1908, 60, 173; Gutbier and Riess, Ber. 1909, 42, 3905). Rubidium also forms compounds containing a larger number of halogen atoms, such as $RbBr_3$, $RbClBr_2$, $RbCl_4I$, &c. (Herty and Black, Amer. Chem. J. 1896, 18, 847; Zeitsch. physikal. Chem. 1899, 28, 523; Abegg, Zeitsch. anorg. Chem. 1906, 50, 403; Foote and Chalker, Amer. Chem. J. 1908, 39, 561).

Rubidium ammonium bromide $RbBr+3NH_4Br$ is a white or yellowish crystalline powder which is recommended as a substitute for potassium bromide as an anti-epileptic and as a hypnotic (Laufenauer, J. Soc. Chem. Ind. 1890, 650, 888; Coblentz, *ibid.* 1898, 736).

Rubidium iodide RbI combines with thiocarbamide to form a crystalline compound $(CSN_2H_4)_4$, RbI, m.p. 202° (Atkins and Werner, Chem. Soc. Trans. 1912, 101, 1177).

Rubidium hydrogen fluoride RbF,HF is partially converted into rubidium fluoride, RbF, when heated with excess of ammonium hydrogen fluoride (Chabrie and Bouchonnet, Compt. rend. 1905, 140, 90; Eggeling and Meyer, Zeitsch. anorg. Chem. 1905, 46, 174).

Rubidium chlorate and *perchlorate*, *rubidium iodate* $RbIO_3$ (Wheeler, Amer. J. Sci. 1902, [iii.] 44, 123; Barker, Chem. Soc. Trans. 1908, 15), and the *periodate* $RbIO_4$ (Barker, *l.c.*) also exist. *Rubidium bromate* (Buell and McCrosky, J. Amer. Chem. Soc. 1921, 43, 2031). The *sulphate* (Silliman, Amer. J. Sci. 12, 30), *sulphites* (Morgan and Smith, Chem. Soc. Trans. 1921, 1069), *nitrate* (Jones, Chem. Soc. Trans. 1908, 1742), *nitrite* (Ball and Alram, Chem. Soc. Trans. 1913, 103, 2130), *trithionate* $Rb_2S_3O_6$ (Mackenzie and Marshall, *ibid.* 1735; Meyer and Eggeling, Ber. 1907, 40, 1351), *chromate* and *dichromates* (Schreinemakers and Filippo, Chem. Zentr. 1906, i. 1321; Wyrouboff, Bull. Soc. chim. 1908, [iv.] 3, 7; Stortenbeker, *ibid.* 481), *rubidium magnesium chromate* $Rb_2Mg{\cdot}(CrO_4)_2 6H_2O$ (Barker, Chem. Soc. Trans. 1911, 1326), *carbonates* and *percarbonates* (Peltner, *l.c.*; Forcrand, Compt. rend. 1909, 149, 97, 719), some *molybdates* (Herschfinkel, Zeitsch. anorg. Chem. 1909, 64, 263; Wempe, Zeitsch. anorg. Chem. 1912, 78, 298), *arsenates* (Bouchonnet, Compt. rend. 1907, 144, 641), *tungstates* (Schaefer, Zeitsch. anorg. Chem. 1904, 38, 142), various *phosphates* (Berg. Ber. 1901, 34, 4181), *tellurates* and *selenates* (Norris and Kingman, Amer. Chem. J. 1901, 26, 318), and *selenodithinate* $Se(SO_3Rb)_2$ (Morgan and Smith, Chem. Soc. Trans. 1921, 1068), *nickel rubidium selenate* $Rb_2Ni(SeO_4)_2,6H_2O$ (Tutton, Phil. Trans. 1917, A. 217, 199), have been prepared.

Rubidium pentasulphide Rb_2S_5 is formed by warming the monosulphide with powdered sulphur and aqueous alkali hydroxide in an atmosphere of hydrogen. It crystallises in dark-red rhombic prisms, m.p. 223°–224° (Biltz and Wilke-Dörfurt, Ber. 1905, 38, 123). Other sulphides and hydrosulphides also exist (Zeitsch. anorg. Chem. 1906, 48, 297 ; *ibid.* 50, 67 ; Rengade and Costeanu, Compt. rend. 1914, 158, 946).

Rubidium phosphide Rb_2P_5 is a reddish-brown solid (Hackspill and Bossuet, Compt. rend. 1912, 154, 209).

Rubidium ammonia $Rb.NH_3$ is prepared by the direct action of liquid ammonia on the metal at about −70° or of the gas at −3° ; its solution in liquid ammonia is used for the preparation of the carbide (Moissan, Compt. rend. 1903, 136, 1177).

Rubidium cyanide RbCN is very soluble in water but insoluble in alcohol and ether. Forms a double salt $RbAg(CN)_2$ with silver cyanide. *Rubidium ferrocyanide* crystallises with $3H_2O$; the *ferricyanide* and *manganicyanide* are anhydrous and isomorphous with the potassium salts (Meyer, Zeitsch. anorg. Chem. 1921, 115, 203).

Rubidium acetylide acetylene $C_2Rb_2C_2H_2$ forms transparent hygroscopic crystals, m.p. 300°, which decompose with the formation of *rubidium carbide* C_2Rb_2 and acetylene (Moissan, Compt. rend. 1903, 136, 1217, 1522).

Rubidium syngenite $CaRb_2(SO_4)_2H_2O$ is obtained when finely divided gypsum is left in contact with a 30 p.c. solution of rubidium sulphate (D'Ans and Zeh, Ber. 1907, 40, 4912).

Rubidium forms *alums* with indium, vanadium, titanium, and iridium.

Iron rubidium selenium alum

$$Rb_2Fe_2(SeO_4)_4,24H_2O$$

separates as pale violet crystals when rubidium carbonate is added to a solution of ferric hydroxide in excess of selenic acid. It has a sp.gr. 2·1308 at 15° and melts in its water of crystallisation at 40°–50°, forming a red liquid (Roncagliolo, Gazz. chim. ital. 1905, [ii.] 35, 553).

When a very dilute solution containing calcium chloride and potassium ferrocyanide is heated at 50° and mixed with a dilute solution of a rubidium or cæsium salt, a precipitate forms which may be collected and washed with 60 p.c. alcohol until free from chlorides. In the case of calcium and cæsium, the precipitate, after being dried at the ordinary temperature, has a composition corresponding approximately with the formula $Cs_4Ca_2Fe_2(CN)_{12},H_2O$. Similar compounds are formed when magnesium chloride is used in place of calcium chloride and potassium ferricyanide in place of potassium ferrocyanide (E. Marmann, Oesterr. Chem. Ztg. 1923, 26, 140 ; Chem. Soc. Absts. 1924, 126, i. 20).

For the spark spectrum of rubidium, *see* H. Reinheimmer (Ann. Physik. 1923, [iv.] 71, 162–177).

RUBIHYDRAN, RUBIRETIN *v.* MADDER.

RUBIJERVINE *v.* CEVADINE.

RUBRESCIN. A substance prepared by melting resorcinol with chloral hydrate. Dissolves in water giving a red solution, which is exceedingly sensitive to alkalis. Used as an indicator.

RUBRESERINE *v.* ORDEAL BEAN.

RUBRIC LAKE. *Madder lake v.* PIGMENTS.

RUBY *v.* CORUNDUM ; also ALUMINIUM.

RUBY-BLENDE *v.* ZINC-BLENDE.

RUBY-COPPER-ORE *v.* CUPRITE.

RUBY-SILVER-ORE *v.* PROUSTITE AND PYRARGYRITE.

RUBY SULPHUR. *Realgar, Arsenic sulphide, v.* ARSENIC.

RUDDLE *v.* HÆMATITE.

RUE, OIL OF, *v.* OILS, ESSENTIAL.

RUFIGALLIC ACID or **RUFIGALLOL** *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

RUFIOPIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

RUM is an ardent spirit, the product of distillation of saccharine matter derived from the sugar-cane. It is usually made from molasses, or from the skimmings of the sugar boilers and the waste of the crushing-house, or (when the cost of production of sugar makes it profitable) from the sugar-cane. The principal source of supply is the West India Islands and British Guiana, and the quality most esteemed is associated with the name of Jamaica. It is also distilled in France from beetroot.

The term 'rum' is by some thought to be derived from the final syllable of 'saccharum.' It is certain, however, that so long ago as 1650 this spirit was known in the West Indies as 'rumbullion,' an old Devonshire term for an uproar, disturbance, or tumult, the word being subsequently contracted into 'rum.' An old writer of that period, speaking of Jamaica, states, 'The chief fudling they make in this island is "rumbullion," alias "kill-devil," and this is made of suggar canes distilled, a hott, hellish, and terrible liquor.' It is well known that many Devonshire colonists settled in the West Indies, and the term 'rumbowline' is said still to linger amongst certain seafaring men in referring to grog. The earliest official mention of this spirit under the name of 'rum' appears to be in an order of the Governor and Council of Jamaica dated July 3, 1661.

The rums of Jamaica and Demerara (British Guiana) represent the two principal types of rum in commerce, the different characters of these being due not only to the nature of the soil and therefore of the products from the sugar-cane, but also to differences in the methods of fermentation, distillation, and mode of manufacture generally.

In the first type the wash is set at a relatively high density (from 1072 to 1096), and the fermentation is slow, lasting from a week to a fortnight, or even longer, whilst in the second the wash is set at a low density (about 1060), and the fermentation lasts only from 30 to 48 hours. In Jamaica, moreover, pot-stills only are used, whilst in other West India Islands, in Trinidad, and British Guiana patent stills are commonly employed, the former resulting in a comparatively low, and the latter a relatively high, production of alcohol.

The following account of the manufacture of Jamaica rum was given before the Royal Commission on Whisky and other Potable Spirits by Mr. Nolan, Special Commissioner of the Jamaica Government to the United Kingdom : 'Jamaica rum is made from sugar-cane in the old pot-still. The sugar-canes, when ripe, are

cut and carted into the works (the canes ripen in from 12 to 15 months). They are passed through a strong steel or iron three or five roll mill worked by steam. The juice of cane liquor falls through the rolls on to a receptacle directly under the mill, which is called the mill-bed. The liquor is carried from the mill-bed by gravitation to another receptacle, which is called the well. From this well it is pumped to large iron vessels called siphons or clarifiers which contain from six to seven hundred gallons. In the bottom of the siphons there are copper steam coils or tubes, which are filled with steam when the siphon is full. The liquor is thus heated to a few degrees below boiling-point. By this means all the scum comes to the top, and the rest of the liquor in the siphon is partially clarified. The clarified liquor is then gradually drawn off by a cock at the side of the siphon low down, until the scum alone is left. The clarified liquor is either sent to the boiling-house to make sugar or passed through other vessels to clarify to a higher degree, as really the whole process of sugar-boiling is to eliminate foreign matters (which take the form of scum) from the liquor, and then remove the water by evaporation. The scum or dirty liquor which remains in the siphon is then drawn off and sent to the still-house, where it is allowed to remain for a few days till it sours. The siphons are also washed out with water, and such water is sent to the same receptacle in the still-house. In fact, all the washings and scums from vessels in the boiling-house are sent to this receptacle. There is also put into this receptacle at the beginning of crop a certain amount of megass (the fibrous part of the cane which remains after crushing the juice from the cane in the mill), which assists to sour the liquor. In the meantime the clarified liquor in the boiling-house is made into sugar and allowed to cool. It is then passed through centrifugals, or purgers, which separate the molasses from the dry sugar on somewhat the same principle as a milk separator. The molasses are then rich, and at this point are sent to the still-house. The only other ingredient used in the manufacture of Jamaica rum is *dunder*. This is a substance which remains at the bottom of the pot-still after all the spirits and a great quantity of the water have been evaporated by distillation from the wash. It is removed from the still and allowed to cool for a few days. It comes from the still with something like the consistency and colour of pea-soup. There are three ingredients, with water used in the setting up of the wash for fermentation, all of which are the products of sugar-cane, viz. scum or skimmings, molasses and dunder. They are used in proportions according to the judgment and practical experience of the distiller, who is guided by all circumstances connected with the estate and distillery. The fermentation is from six to twelve days, in some cases longer. After the fermentation subsides, the wash is pumped into a pot-still. Jamaica has at all times used the pot-still; and there is no other used in the island.'

Until comparatively recently the fermentation process was left very much to chance, but, commencing in 1903, special investigations have been, and are still being, made in Jamaica into the chemistry and bacteriology of the manufacture of rum, with special reference to the micro-organisms concerned in the fermentation processes, and their influence on the character, quality, and flavour of the rum. It was found that the peculiar and characteristic flavour of Jamaica rum was largely due to acidic and putrefactive fermentation by bacteria.

According to Cousins (West India Bulletin, vol. 8, No. 1, 1907), there are three classes of Jamaica rum, viz. (1) 'local trade quality,' for home consumption; (2) 'home-trade quality,' for consumption in the United Kingdom; and (3) 'export trade quality,' for exportation to the Continent of Europe.

The rums of the first class have usually a lower ester content (sometimes as low as 90 parts per 100,000) than the second, and an inferior flavour. They are the result of light settings and quick fermentation. The stills are heated by steam coils and double retorts are used. These rums constitute the 'wine of the country,' and are consumed almost exclusively by the lower orders in the island.

The second class, sometimes described as 'public-house rums' are those exported to and usually known in the United Kingdom as 'Jamaica rum.' This constitutes the bulk of the rum exported from Jamaica.

The flavour of these is characterised by a heavy residual 'body,' due mainly to esters of acids of high molecular weight. These acids are not producible from sugars, and are almost absent in rums other than Jamaican, produced from diluted molasses without dunder or acid skimming and distilled in patent stills. Investigations made in the Government Agricultural Department in Jamaica indicated that the higher acids result from the bacterial decomposition of the dead yeasts found in the distilling materials.

The best types of these 'home-trade' rums contain from 300 to 500 parts of esters, and the bulk of the rums of this class about 200 parts per 100,000, but in some cases the ester content even of genuine home-trade rums of good quality falls as low as 100.

These rums are generally produced by a slower type of fermentation than the 'local trade' rums, the fermentation period sometimes extending over a fortnight, although even this is not so prolonged as the fermentation period of the export rums described below.

As compared with the 'local trade' rums, they have a fuller and more fruity aroma, and on dilution the spicy residual flavour is more strongly marked. The latter is due to the larger proportion of higher alcohols present, and these, in excess, are apt to cause an objectionable cloudiness on dilution. The remedy for this is to test the spirit with water before accepting it as rum, retaining a cloudy distillate for further distillation, and the fermenting vats should be limed to secure a clearer fermentation. Another defect sometimes observed in these rums is a burnt flavour (best detected on dilution with water) due to the use of a 'direct fire' still, and the remedy in this case is to heat the stills with a copper coil. A 'fruity' aroma is sometimes obtained by the addition of pine-apples or guavas to the wash in the still.

The rums of the third class, or 'export

trade,' quality differ much more widely from the 'local' and 'home trade' rums than these do from each other. Rums of this type are characterised by an abnormally high proportion of esters, and are exported mainly to the Continent of Europe, principally to Germany. They are not suitable for direct use as a beverage, but are blended together and vatted off with lighter rums or even with neutral spirit to impart to the latter a rum character. They are also used to fortify and give body to hock and similar wines.

These 'export' rums, or 'German-flavoured,' as they are commonly called in Jamaica, are produced on the north side of the island on comparatively small estates where, owing to certain disadvantages under which they labour as sugar-producing estates, it is more profitable to manufacture rum than sugar.

Instead of 30 hours' fermentation, which suffices for certain rums of the Demerara or Trinidad type (*v. infra*), these 'German-flavoured' rums require a fermentation period lasting from a fortnight to three weeks, and the process is conducted in a strongly acid wash. The organisms are of the fission type, and are able to attenuate a liquor with an acidity of 3 p.c., whilst the ordinary oval budding yeast is paralysed by an acidity of less than one-fifth of this amount.

The proportion of esters in these rums is relatively very high, varying from 500 to 1200, and in some instances reaching 1500 or more parts per 100,000. According to Cousins, about 97 p.c. of these esters consist of acetic ester and 2 p.c. of butyric ester; traces of formic ester may be present, and from $\frac{1}{2}$ to $\frac{3}{4}$ p.c. of the total consists of heavy esters derived from acids of high molecular weight. It is upon the latter that the character and to a large extent the commercial value of the rum is said to depend.

The acetic and butyric esters may be considered merely as media for the conveyance of the aroma of the heavier esters, which are best recognised by smell after diluting with water, thereby reducing the vapour tension and pungency of the more volatile esters. The latter are best appreciated before diluting the spirit.

A process for reinforcing the content of the natural esters of rum by recovering the volatile acids left in the spent liquor from the retorts and using them in a subsequent operation has been carried out on a commercial scale by Cousins. The acids in the lees are fixed with lime, the residue evaporated to dryness, and the acids liberated by the requisite amount of sulphuric acid, recovered by distillation, and returned into the process. By this means rums containing as much as 3500 parts of esters per 100,000 have been obtained. The process appears to be equally applicable to brandy and whisky.

Pot-still rum when new has a rather disagreeable odour, but the true characteristic flavour develops by storing in wooden casks, and continues to improve for eight or ten years. Rum matures more rapidly, however, than either brandy or whisky.

The rum of British Guiana, usually known as 'Demerara' rum, is made almost exclusively from vacuum pan molasses with the occasional addition of other sugar-containing waste products of the sugar factories.

The following account of Demerara rum, as made in British Guiana, is taken from a statement drawn up by the British Guiana Planters' Association and transmitted to the Royal Commission on Whisky and other Potable Spirits, 1909:—

'In British Guiana the wash (wort) is prepared by diluting molasses with water to a density of 1060, and rendered slightly acid by the addition of sulphuric acid in quantity sufficient to set free more or less of the combined organic acids, but so as not to have uncombined sulphuric acid present in the wash; whilst in some of the distilleries additions of sulphate of ammonia in small proportions are made to the wash, in order to supply readily available nitrogenous food for the yeasts and thus to enable them to multiply with rapidity and to retain a healthy active condition. The reason for rendering the wash slightly acid is to guard against the excessive propagation of the butyric and lactic organisms and to render it more suitable for active alcoholic fermentation. Within a very short time from the molasses being diluted it enters into vigorous fermentation, and the fermentation rapidly proceeds to complete attenuation.

'In British Guiana the distilleries are of three kinds: (1) those using pot-stills or vat-stills, which are practically only modified pot-stills; (2) those using both pot-stills or vat-stills and Coffey or other continuous rectifying stills; and (3) those using only Coffey or other continuous rectifying stills. Out of forty-two distilleries in operation, thirty-two use pot- or vat-stills only; three have both pot- or vat-stills and continuous stills; whilst seven possess continuous stills only.

'Vat-stills consist of cylindrical wooden vessels built of staves strongly hooped with wrought-iron. They have high copper domes covering openings in the heads of the vessels which communicate with a retort or retorts of the Jamaican pattern, but as a rule the retort acts as the lowest vessel of a rectifying column. As in Winter's still, a spiral pipe or a series of small perpendicular pipes descend down the interior of a column through which cold water is run whenever distillation is in progress, and by which the spirit vapour undergoes a process of rectification as it ascends the column before passing into the condenser. The vat-stills are heated by injection of steam. The Coffey or continuous rectifying stills are of the usual well-known types.'

By means of the patent stills some of the estate distilleries in British Guiana are able to produce approximately one proof gallon of spirit for each five degrees of attenuation from every hundred gallons of wash, or about 90 p.c. of the theoretical yield. The greater part of the patent still spirit is consumed locally, and this local preference for the lighter types of rum obtains in other West Indian colonies, and has already been noticed in connection with the 'local trade' rum of Jamaica.

Compared with Jamaica rums, the proportion of esters in rums of the Demerara type is very low, but varies considerably. The results of determinations, made in the Government

Laboratory of British Guiana, of the esters (calculated as ethyl acetate) in over 400 samples of rum examined during the years 1901–1908, showed a minimum of 63 and a maximum of 104 with an average of 81 parts per 100,000 of absolute alcohol by volume.

According to Girard and Cuniasse (Analyse des Alcools et des spiritueux), the average proportion of esters and other secondary products comprised in the 'coefficient non-alcohol' (*v.* BRANDY) found in ordinary rums of commerce known to be genuine, are shown in the following table expressed in relation to 100,000 parts per volume of absolute alcohol :—

	Min.	*Max.*	*Average.*
Acidity (as acetic acid) .	158·4	400·0	250·8
Aldehydes (as acetic aldehyde)	0·3	54·5	24·4
Furfural	1·2	50·0	7·1
Esters (as acetic ester) .	105·7	443·1	229·5
Higher alcohols (*iso*butyl standard) . . .	52·0	308·6	140·4
Coefficient of secondary products	432·7	919·0	652·5

Sanarens (Ann. Falsif. 1913, 6, 488) has published the results of analyses of numerous samples of authentic rums : *cf.* Analyst, 1913, 501.

An important research on the composition of 'Deutscher Rum,' by Mezger and Gesser, was published in 1921 (Zeit. für angew. Chem. 1921, No. 101).

Details of methods for determining the secondary products may be found in the Minutes of Evidence taken by the Royal Commission on Whisky and other Potable Spirits, 1909 (vol. 2, Appendix Q, xii.).

The colouring matter usually employed consists of caramel made from burnt molasses or sugar, but care should be exercised in its use so as to avoid excessive 'obscuration' or apparent diminution of strength as shown by the hydrometer or alcoholometer. The 'obscuration' should not exceed 1½ p.c. of proof spirit, and the tint of a fully coloured rum should correspond with about No. 19 on Lovibond's tintometer.

The strength of rum as imported into the United Kingdom varies from about 20 underproof to 50 or more overproof, the average being 35 overproof, equivalent to 77 p.c. of absolute alcohol by volume. The lowest limit of strength for the sale of rum under the Food and Drugs Acts is 25 underproof unless the fact of its dilution to a lower strength is declared. During the war, however, the maximum strength at which rum and other spirits could be sold for use as a beverage was fixed at 30 u.p. and dilution was permissible down to 50 u.p.

The British Customs distinguish between rums from Jamaica, rums from other sugar-cane producing countries, and 'imitation' rums, a term applied to spirits of rum character, imported from countries in which the sugar-cane is not cultivated.

The quantity of the latter imported is insignificant compared with genuine rum, and during the decade 1900–10 it declined from about 44,000 proof gallons in 1900 to not more than 6000 proof gallons in 1910, and then remained stationary until 1914, when an abnormal increase took place owing to the demand for spirit in connection with the war. Since the war, the importations of 'imitation' rum have dwindled almost to vanishing point, the quantity recorded last year (1922) being only 363 proof gallons. The quantities of genuine rum imported during the same periods were over 4,000,000 proof gallons in 1900 and nearly 3,000,000 proof gallons in 1910. Of this, about two-thirds came from British Guiana ('Demerara' rum) and about one-quarter from Jamaica. The sudden increase during the war, reaching 10,000,000 proof gallons in 1915 and 1916, was followed by a rapid falling off, until, in 1922, the total quantity imported was only 1,500,000 proof gallons, of which about one-half came from Jamaica, and about one-quarter from British Guiana and the Union of South Africa respectively.

The proportion of rum consumed per head in the United Kingdom has gradually declined (in common with other spirituous liquors, including beer and wine) during the decade above referred to, being in the case of rum equivalent to 0·11 gallon per head of the population in 1900 as compared with 0·05 gallon, or less than half the quantity, per head in 1910, and at the present time (1923) is approximately only 0·04 gallon per head.

'*Imitation rum*' is made either by the addition of heavily flavoured rums rich in esters or artificial 'essence of rum' (*v. infra*) to plain spirit from potatoes or beet molasses, with addition of colouring matter.

As an example of an artificial rum '*essence*' the following is given by Fleischman (The Art of Blending and Compounding Liquors and Wines). A mixture consisting of 32 ozs. of alcohol, 4 ozs. of sulphuric acid, 2 ozs. of manganese dioxide, and 4 ozs. of pyroligneous acid is distilled, and to 32 ozs. of the distillate are added 32 ozs. of acetic ester, 8 ozs. of butyric ester, 16 ozs. of saffron extract, and $\frac{1}{8}$ oz. of oil of birch.

Rum shrub is rum flavoured with orange and lemon and sweetened with sugar. It may be made on a small scale from the following recipe : To 1 gallon of rum add 1 pint each of orange and lemon juice and the peels of two oranges and one lemon. Digest for 24 hours in the cold, strain, and sweeten with a syrup made by dissolving 4 lbs. of white sugar in 5 pints of water.

West India shrub is very similar to the above, the orange and lemon juice being replaced by an equal quantity of lime juice. J. C.

RUMEX ECKLONIANUS, Meisner (N. O. Polygonaceæ). A herb indigenous to South Africa, where it is reputed to possess medicinal properties. Contains ceryl alcohol, a phytosterol, $C_{20}H_{34}O$, apparently identical with rhamnol, palmitic, stearic, oleic, linolic, and *iso*linolenic acids ; a small amount of ipuranol, $C_{23}H_{38}O_2(OH)_2$; kæmpferol, chrysophanic acid, emodin, and emodin monomethylether, together with traces of other crystalline substances and large amounts of inorganic salts. The emodin monomethylether is identical with that obtained by Perkin and Hummel from *Ventilago madraspatana* (Chem. Soc. Trans. 1894, 65, 932). The extract from this plant possesses a mild purgative action (Tutin and Clewer, Chem. Soc. Trans. 1910, 97, 1).

A. G. P.

RUMEX NEPALENSIS. According to Hesse (Ann. 1899, 309, 32), the root of *Rumex nepalensis* (Wall) contains chrysophanic acid and *nepodin* $C_{18}H_{16}O_4$.

Nepodin $C_{18}H_{16}O_4$, the main constituent of the root, greenish-yellow prisms, m.p. 158°, soluble in solutions of the alkali carbonates. The *diacetyl* compound forms pale yellow rhombohedra which darken at 180°, and melt with decomposition at 198°.

The root of *Rumex palustris* contains chrysophanic acid and nepodin, which are also present in *Rumex obtusifolius*, along with *lapodin* $C_{18}H_{16}O_5$, which crystallises in yellow needles and melts at 206° with decomposition.

For constituents of the root of *Rumex crispus*, *see* Beal and Okey (J. Amer. Chem. Soc. 1919, 41, 693) and Murayama and Itagaki (J. Pharm. Soc. Japan, 1921, 327). A. G. P.

RUSSET RUBIATE. *Rubens madder v.* PIGMENTS.

RUTHENIUM. Sym. Ru. At.wt. 101·65. This metal is obtained, together with osmium, as a by-product in the treatment of osmiridium and other native alloys of the platinum metals. It is the rarest of the platinum metals and was discovered in 1844 by Claus in the residues of Uralian platinum.

The residue from the extraction of iridium and osmium is heated with a mixture of potash and potassium nitrate in a silver crucible. After cooling, the brown mass is extracted with water, an orange solution of potassium ruthenate being formed. It is separated by decantation and the ruthenium salt is precipitated by means of nitric acid or alcohol. It is washed, dried, and reduced by hydrogen. The metal thus obtained, which is impure, is again melted with potash and nitre; it is then treated with chlorine, when volatile ruthenium peroxide is formed, which is redistilled with water in a current of chlorine. The peroxide is then converted into oxide or trichloride, which when reduced with hydrogen gives the pure metal (Claus, Ann. Chim. 1860, [iii.] 59, 111). The metal may be obtained crystalline by heating its alloy with tin in a carbon crucible, in a current of hydrogen chloride, or by heating the finely divided metal with pyrites and borax (*v.* Deville and Debray, Compt. rend. 1879, 89, 590).

Ruthenium may be purified by dissolving the chloride, or double ammonium chloride, in *aqua regia* and boiling with ammonia until the solution becomes clear yellow. Evaporation yields yellow crystals of a nitroso-ammine. The solution of this in boiling water gives a yellow crystalline double salt with mercuric chloride, almost insoluble in cold water but soluble in boiling water from which it may be recrystallised (Werner, Ber. 1907, 40, 2614).

Wolcott Gibbs separates ruthenium in solution, as stated under Platinum, by forming the double potassium nitrite and extracting the dried mass with absolute alcohol in which the ruthenium potassium nitrite alone is soluble. A few drops of colourless ammonium sulphide added to the solution of this salt in alcohol or water give a magnificent crimson colour which serves as a delicate test for ruthenium.

Claus detects ruthenium in an iridium solution by adding excess of caustic potash. Pure iridium is decolorised at once, but if ruthenium is present the solution does not go colourless and soon becomes turbid with a red-brown coloration.

Carey Lea's test for ruthenium is very sensitive and trustworthy. The solution is made ammoniacal, boiled and filtered. A few crystals of sodium thiosulphate are added and the boiling continued. Ruthenium, if present, causes the liquor gradually to turn pink or deep claret colour if much is present. This test is interfered with by the presence of palladium, and copper or nickel must not be present (Amer. J. Sci. [2], 44 (1867), 222).

Ruthenium is white, hard, and brittle, and, after osmium, is the least fusible but the most readily oxidised metal in the group. It melts at 2450°. The fused metal has a sp.gr. of 12·06 and is scarcely attacked by acids or even by *aqua regia*. It forms workable alloys with platinum and palladium which are of little commercial importance owing to the scarcity of the metal.

At a bright red heat it is oxidised superficially by air or oxygen. It is also attacked by chlorine and by fluorine, but not by sulphur.

In a fine state of division the metal has energetic catalytic properties.

Colloidal ruthenium has been obtained in the same manner as colloidal osmium (*v.* OSMIUM).

Neither the metal nor its salts have found any definite application in the arts.

For the spectrum of Ruthenium, *see* Paulson (Ann. Physik. 1915, (iv.) 46, 698; Physikal Zeitsch. 1915, 16, 352); Kail (Chem. Zentr. 1915, i. 302).

For the *Stereochemistry* of the Ruthenium atom, *see* Werner and Smirnoff (Helv. Chim. Acta, 1820, 3, 737).

RUTHENIUM COMPOUNDS.

Ruthenium forms the oxides Ru_2O_3, RuO_2, RuO_4, and salts corresponding to the oxides RuO_3, Ru_2O_7 (Gutbier and Ransohoff, Zeitsch. anorg. Chem. 1905, 45, 243). For the existence of bivalent Ruthenium compounds, *see* Remy (*ibid.* 1920, 113, 229).

Ruthenium sesquioxide Ru_2O_3 forms a black scaly mass, produced when the trioxide is heated in carbon dioxide. The corresponding trihydroxide $Ru(OH)_3$ is obtained by precipitating the trichloride with an alkali. It is a black-brown precipitate insoluble in water and alkalis, but forming a yellow solution in acids.

Ruthenium dioxide RuO_2 is obtained by roasting the disulphide or sulphate in air or by heating osmiridium alloy in a current of air, when the dioxide is carried forward by the osmium tetroxide formed at the same time, and deposited in the colder part of the tube; the osmium tetroxide being more volatile is carried further. RuO_2 is formed by heating finely divided ruthenium in oxygen to 700°–1000°. Volatile RuO_4 is also formed, at 1200° four thousand times as rapidly as at 700°. Crystals of RuO_2 are also observed in the sublimate (Gutbier and others, Zeitsch. anorg. Chem. 1916, 96, 182). The dioxide crystallises in small hard tetragonal pyramids, possesses a green metallic lustre, a bluish-green iridescence, and is isomorphous with *cassiterite* and *rutile*

The hydroxide $Ru(OH)_4,3H_2O$ is a red-brown substance giving yellow solutions in alkalis and acids.

Potassium ruthenate K_2RuO_4 is obtained by mixing the tetroxide with aqueous caustic potash and keeping at 60° till no more oxygen is evolved, and then evaporating *in vacuô* to crystallisation. It decomposes in air.

Ruthenium tetroxide RuO_4 is prepared by treating a solution of potassium ruthenate (formed by fusing the element with sodium peroxide; or, better, with potash and potassium nitrate) with chlorine (Mylius and Dietz, Ber. 1898, 31, 3187; Gutbier, Zeitsch. angew. Chem. 1909, 22, 487). It forms beautiful crystals, fairly stable when dry, but decomposing rapidly when moist. Its b.p. is just over 100° and its vapour has an irritating smell and is poisonous. It blackens organic matter, and is reduced by alcoholic potash. When the solid tetroxide is treated with alcohol serious explosions may occur (Debray and Joly, Compt. rend. 1891, 113, 693; Gutbier, Zeitsch. anorg. Chem. 1916, 95, 177).

Potassium per-ruthenate $KRuO_4$ is formed by mixing the tetroxide with cold aqueous caustic potash and evaporating *in vacuô*. The solution is unstable. Ammonium ruthenate is formed by adding concentrated ammonia to a concentrated solution of the tetroxide in water. Its composition is $(NH_4)_2RuO_5$.

Ruthenium dichloride $RuCl_2$ is probably present in the blue liquid obtained by the action of sulphuretted hydrogen on the trichloride, but no true double salts have been crystallised.

Ruthenium trichloride $RuCl_3$ is best prepared by treating the tetroxide with 20 p.c. hydrochloric acid, and then placing the whole in a cooling mixture under reduced pressure for 2 hours. It forms an almost black, crystalline mass, and yields an orange-coloured solution in water, which when warmed gently deposits an intensely black precipitate (Gutbier and Trenkner, Zeitsch. anorg. Chem. 1905, 45, 166, 178; Remy, J. pr. Chem. 1920, (ii.) 101, 341). The solid chloride becomes liquid when in contact with the air and dissolves in dilute aqueous or alcoholic hydrochloric acid with an intense purple-red colour (Gutbier, *l.c.*). The trichloride forms double salts with alkali chlorides, known as *ruthenochlorides* or *chlororuthenites* (Miolati and Tagiuri, Gazz. chim. ital. 1900, 30, ii. 511; Howe, J. Amer. Chem. Soc. 1901, 23, 775; *ibid.* 1904, 26, 543, 942). $Na_3RuCl_4,9H_2O$ forms triclinic prisms, melting at 50° in its own water. It is soluble in 1½ parts of water but insoluble in alcohol.

Ruthenium tetrachloride $RuCl_4$ has not been obtained pure; it also forms double chlorides with the alkali chlorides and with hydrochlorides of organic bases, known as *ruthenichlorides* or *chlororuthenates* (Gutbier and Zwicker, Ber. 1907, 40, 690; *ibid.* 1911, 44, 306; also Howe, *l.c.* Both Howe and Joly (Gazz. chim. ital. 1889, 29, 1) failed to obtain $RuCl_4$ or its salts by direct oxidation or chlorination of $RuCl_3$. Those which Claus described were all found to contain oxides of nitrogen. Bromide and iodide derivatives of ruthenium are also known (Gutbier and Krauss, Ber. 1921, 54 [B], 2835).

Ruthenium sulphide Ru_2S_3 occurs naturally as the mineral *laurite* and crystallises in small octahedra (*see* Antony and Lucchesi, Gazz. chim. ital. 1900, 30, ii. 539). For colloidal sulphur compounds, *see* Jaeger and de Boer (Proc. K. Akad. Wetensch. Amsterdam, 1920, 23, 95).

Ruthenic sulphate $Ru(SO_4)_2$ is obtained by dissolving the tetrahydroxide in sulphuric acid. It forms a deliquescent powder closely resembling mosaic gold. It gives a red-yellow solution in water, which when treated with sulphur dioxide changes from bright red to green, then to blue. When alcohol is added to this blue solution colloidal *ruthenium sulphite* $Ru_2(SO_3)_3$ is precipitated (Antony and Lucchesi, *ibid.* 71). By the continued action of sulphur dioxide on ruthenic sulphate, *Ruthenium dithionate* RuS_2O_6 is formed (*ibid.* 1898, 28, ii. 139). For the *alkali ruthenium double sulphites*, *see* Remy (Zeitsch. anorg. Chem. 1922, 124, 248).

H. Remy and C. Breimeyer (Zeitsch. anorg. Chem. 1923, 129, 215) have described the preparation of the double sulphites of ruthenium and the alkali metals: *potassium trisulphitoruthenate* $K_4[Ru(SO_3)_3]$, dark green needles; *sodium undecasulphitodiruthenate*

$$Ru_2(SO_3)_3 8Na_2SO_3,3H_2O$$

yellowish-white crystals; *sodium ruthenoruthenisulphite* $2RuSO_3,Ru_2(SO_3)_3,4Na_2SO_3$, dark blue, amorphous powder (Chem. Soc. Absts. 1924, 126, ii. 54).

Ruthenium nitrosochlorides and some of its complex derivatives are described by Howe (J. Amer. Chem. Soc. 1894, 16, 388); Lind (*ibid.* 1903, 25, 928); Brizard (Compt. rend. 1899, 129, 216; Ann. Chim. 1900, vii. 21, 311).

Ruthenium forms complex compounds with ammonia (Werner, Ber. 1907, 40, 2614; also Gutbier and Gutbier and Krauss, Ber. 1923, 56, [B] 1008). *Rutheniocyanides* corresponding with the ferrocyanides and *rutheniocyanic acid* are described by Howe (J. Amer. Chem. Soc. 1896, 18, 981; Howe and Campbell, *ibid.* 1898, 20, 29); ruthenium carbonyl compounds by Mond, Hirtz, and Cowap (Chem. Soc. Trans. 1910, 798).

Ruthenium carbonyl is formed by acting on the metal with carbon monoxide at 300° with a minimum pressure of 400 atms. It decomposes again on further heating (Mond, Hirtz, and Cowap, Chem. Soc. Trans. 1910, 97, 798). Mond and Wallis (*idem.* 1922, 30) describe a solid brown amorphous carbonyl of the composition $Ru(CO)_2$ soluble in water and insoluble in benzene.

Ruthenium silicide RuSi forms hard, small white crystals of sp.gr. 5·40 (Moissan and Manchot, Compt. rend. 1903, 137, 229).

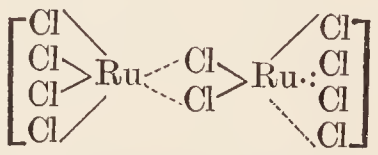
Ruthenium phosphorus halides have been obtained by Strecker and Schurigin (Ber. 1909, 42, 1767).

The following organic derivatives are known: *propylenediammonium-μ-dichloro-octachloro-diruthenate* $[Ru_2Cl_{10}](C_3H_6,N_2H_6)_2$, dark red; the *α-picolinium* salt, black needles; *isoquinolinium* salt, dark red needles and plates; the corresponding bromides of *ethylenediammonium*, black needles; *propylenediammonium*, black; *α-picolinium*, black; *isoquinoliniumhexachlororutheniate*

$$[RuCl_6](C_9H_7NH)_2$$

dark green; the corresponding *triethylammonium*

bromide, dark blue plates; *isoquinolinium bromide*, dark blue. The annexed formula is given for the complex *dirutheniate anion* (A. Gutbier, Zeitsch. anorg. Chem. 1923, 129, 83–88; Chem. Soc. Absts. 1923, 124, i. 1184).



For other organic derivatives, *see* Gutbier and Zwicker (Ber. 1907, 40, 690); Gutbier and Leuchs (*ibid.* 1911, 44, 306); Barbieri (Atti R. Accad. Lincei, 1914, (v.) 23, 1, 334); Gutbier (J. pr. Chem. 1915, (ii.) 91, 103); Werner and Smirnoff (Helv. Chim. Acta, 1920, 3, 737).

A. J. W.

RUTHERFORDINE. Uranyl carbonate $(UO_2)CO_3$ occurring as an earthy, yellow alteration product of uraninite (pitchblende), and still preserving the form of the cubic crystals of the original mineral. It resembles uranium-ochre in appearance; sp.gr. 4·82. The radioactivity of rutherfordine, and also of the associated uraninite, is about 20 p.c. higher than that of pitchblende from Joachimsthal. It is found embedded in sheets of mica in the mica mines of the Uruguru Mountains in the Morogoro district, East Africa. The mineral was named, by W. Marckwald in 1906, after Sir Ernest Rutherford on account of his work on radioactivity. It is not to be confused with the rutherfordite of C. U. Shepard (1851) from Rutherford Co., North Carolina, which is probably identical with fergusonite.

L. J. S.

RUTILE. A native form of titanium dioxide (TiO_2) crystallising in the tetragonal system and isomorphous with cassiterite (SnO_2). Other native forms of titanium dioxide are the less common and less stable minerals anatase and brookite. Rutile forms prismatic crystals which are frequently twinned and have a good prismatic cleavage. It is translucent to opaque, often with a brilliant lustre, and ranges in colour from reddish-brown to black; the streak is yellowish-brown; sp.gr. 4·2; H. = 6–6½. The characteristic reddish-brown colour (hence the name rutile, from the Latin *rutilus*, red) may usually be seen on thin cleavage flakes when the mineral is broken. The range in colour, and also in sp. gr. (4·2–4·5), is due to the presence of variable amounts of iron, probably present as ferrous titanate $FeTiO_3$ in solid solution in the rutile; in the black variety, called *nigrine*, there may be as much as 14 p.c. FeO. In ilmenorutile the sp.gr. rises still higher (*v.* Strüverite). Rutile occurs in granitic rocks, but more frequently in gneiss and schist, and is often aggregated in quartz veins traversing these rocks. Being resistant to weathering agents, it accumulates in sands and clays. Large crystals are found in quartz veins at Graves Mountain in Georgia, in the apatite mines at Kragerö, Risör, and Arendal in Norway, &c. At Roseland in Nelson Co., Virginia, it occurs abundantly in pegmatite, and together with apatite and ilmenite forms a dyke-rock called nelsonite (W. M. Thornton, Amer. J. Sci. 1911, 31, 218). A somewhat similar dyke-rock composed of rutile, ilmenite, and sapphirine occurring at St. Urbain, Quebec, is called urbainite (C. H. Warren, Amer. J. Sci. 1912, 33, 263). These rocks are quarried, crushed, and washed, and the rutile obtained in the form of a resinous brown sand (TiO_2 95 p.c.). Small amounts of the mineral are also produced commercially in Norway and Talunga in South Australia. Rutile is the richest and purest mineral as a source of titanium (Ti 60·05 p.c.), although larger amounts are available in ilmenite and titaniferous iron-ores. It is used in the manufacture of ferro-titanium and titan-steel, and copper and manganese alloys; for imparting a yellowish tinge of colour to glass and porcelain (particularly for false teeth); in dyeing leather; and in the 'carbons' of electric arc-lights. Rutile is occasionally cut as a gem-stone; with its dark colour and high adamantine lustre, it somewhat resembles black diamond. Quartz (rock-crystal) enclosing fine needles and hairs of yellowish-brown rutile is cut under the name 'Venus's hair.'

References.—The Distribution and Uses of Titanium Ores (Bull. Imp. Inst., 1917, 15, 82); T. L. Watson, The Rutile Deposits of the Eastern United States (Bull. U.S. Geol. Survey, 1914, No. 580); T. L. Watson and S. Taber (Bull. Virginia Geol. Survey, 1913, 3 A).

L. J. S.

RUTIN *v.* Glucosides.

Rutin and sophorin are identical substances, the formula being $C_{33}H_{42}O_{20},4H_2O$. They are hydrolysed by the enzyme rhamninase, which occurs in seeds of *Rhamnus infectoria* and *R. cathartica*. This enzyme does not exist in the buds of *Sophora japonica* or the leaves of *Ruta graveolens*, the sources of the glucoside. The sugar produced on hydrolysis is rhamninose, $C_{18}H_{32}O_{14}$ (H. ter Meulen, Rec. trav. chim. 1923, 42, 380–386; J. Soc. Chem. Ind. 1923, 42, 678 A).

RYE *v.* Cereals.

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